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BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN

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Vol. 32 No. 8 August 1959

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Published by the Chemical Society of Japan

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(NIPPON KAGAKUKAI)

Founded in 1948

Successor to the former Chemical Society of Japan founded in 1878 and to the Society of Chemical Industry, Japan founded in 1898.

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*On the Mechanism of Oxidation by Cuprous Chloride, Pyridine and Air. I. The Properties of the Reaction**

By Keizō KINOSHITA

(Received September 30, 1958)

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It was previously reported that by aerial oxidation catalyzed by cuprous chloride in a pyridine solution, benzoin was primarily converted into benzil, which was further oxidized to benzoic acid almost quantitatively[1]. In this reaction, "oxidant A", a product of aerial oxidation of cuprous chloride pyridine complex, is considered to be the actual oxidant[2]. On the other hand, with cupric chloride as a catalyst, no benzoic acid is obtained, although benzoin is converted into benzil almost quantitatively[1].

$$\underset{\text{Benzoin}}{C_6H_5CHOHCOC_6H_5} \xrightarrow[\text{Air}]{Cu_2Cl_2+\text{Pyridine}} 2C_6H_5COOH \quad (1)$$

$$C_6H_5CHOHCOC_6H_5 \xrightarrow[\text{Air}]{CuCl_2+\text{Pyridine}} \underset{\text{Benzil}}{C_6H_5COCOC_6H_5} \quad (2)$$

Terent'ev et al.[3] reported that by aerial oxidation catalyzed by cuprous chloride in a pyridine solution, aromatic amines were converted into the corresponding azo compounds, but that with cupric chloride as a catalyst, these azo compounds were never obtained.

$$2C_6H_5NH_2 \xrightarrow[\text{Air}]{Cu_2Cl_2+\text{Pyridine}} C_6H_5N=NC_6H_5 \quad (3)$$

This paper describes the properties of these reactions.

Experimental

Materials.—Benzil was prepared by oxidation of benzoin with nitric acid, and recrystallized from alcohol, m.p. 94~95°C[4]. Aniline (b.p. 184~185°C) was redistilled immediately before use. Cuprous chloride was prepared by reduction of cupric chloride with sodium sulfite[5], washed with acetone and dried.

(1) Aerial Oxidation of Aniline Catalyzed by Cuprous Chloride in a Pyridine Solution.—A mixture of aniline (2.0 g., 2.2/100 mol.), cuprous chloride (2.0 g., 1/100 mol.) and pyridine (50 cc.) was stirred in a stream of air for 5 hr. at room temperature. The resulting mixture was acidified with 6N-H_2SO_4, and extracted with ether (500 cc.). After removal of the ether, the residue was extracted with light petroleum (b.p. 40~60°C), and chromatographed on activated alumina (Wako Pure Chemical Industries, Ltd.). Azobenzene (1.2 g., 60%) was obtained; m.p. 67~68°C. (Lit. 68°C). It was identified with azobenzene by a mixed melting point determination and an analysis.

Anal. Found: C, 79.27; H, 5.57; N, 15.36. Calcd. for $C_{12}H_{10}N_2$: C, 79.12; H, 5.49; N, 15.38%.

(2) Oxidation of Aniline in the Absence of Air.—Cuprous chloride (8.0 g., 4/100 mol.) in pyridine (100 cc.) was oxidized with air for 3 hr. at room temperature. A mixture of aniline (2.0 g., 2.2/100 mol.) and "oxidant A" thus prepared, was stirred for 5 hr. at room temperature in a stream of nitrogen. The resulting mixture was acidified with 6N-H_2SO_4 and extracted with ether. White precipitate remained. From the ether solution, azobenzene (0.5 g.) was obtained as in Experiment 1; m.p. 67~68°C, its melting point was not depressed on admixing with an authentic sample. A trace of red substance remained on top of the activated alumina.

The color of the aqueous layer was at first pale blue, but after the solution was kept in air its color turned to darker blue. The white precipitate was dissoluble in an aqueous ammonia solution. The color of the ammonia solution kept in air turned to blue. These results suggest that cuprous chloride was produced during the oxidation of aniline.

(3) Attempted Aerial Oxidation of Aniline in the Presence of Acetic Acid.—A mixture of aniline (2.0 g., 2.2/100 mol.), cuprous chloride (2.0 g., 1/100 mol.), acetic acid (1.8 g., 3/100 mol.) and pyridine (100 cc.) was treated as in Experiment 1. A trace of red substance remained on top of the activated alumina, and no other neutral substance was obtained. The color of the aqueous solution was blue.

(4) Reaction of Cupric Chloride Pyridine Complex with Potassium Hydroxide.—(a) Cupric chloride (3.4 g., 2/100 mol.) was refluxed in pyridine (50 cc.) until all the precipitate was turned into blue needles. Potassium hydroxide (1.1 g., 2/100 mol.) in methyl alcohol (50 cc.) was added dropwise under stirring to the cooled pyridine solution of cupric chloride pyridine

* The present work was presented partly at the Symposium on the Mechanism of Organic Chemical Reaction of the Chemical Society of Japan, held at Osaka in October, 1955, and partly at the similar symposium of the same society, held at Nagoya in October, 1957.

1) K. Kinoshita, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **75**, 48 (1954).

2) K. Kinoshita, ibid., **75**, 173 (1954).

3) A. P. Terent'ev et al., *Doklady Akad. Nauk U. S. S. R.*, **1955**, 91—93. [*Chem. Abstr.*, **50**, 4807 (1956).]

4) R. Adams, "Organic Syntheses", Vol. I, John Wiley & Sons, Inc., New York (1921), p. 25.

5) W. C. Ferdnelius, "Inorganic Syntheses", Vol. II, McGraw-Hill, New York (1946), p. 1.

complex. The color of the resulting mixture was green.

(b) When potassium hydroxide (1.1 g., 2/100 mol.) in methyl alcohol (50 cc.) was added to the copper complex prepared in Experiment 4a, pale blue precipitate was formed from the green solution.

(5) Oxidation of Benzil with the Copper Complex Prepared in Experiment 4.—(a) A mixture of benzil (2.0 g., 1/100 mol.) and the copper complex prepared in Experiment 4a was stirred at 30°C for 2 hr. in a stream of air. The resulting mixture was acidified with 6N-H_2SO_4, and extracted with ether (500 cc.). The ethereal layer was extracted with aqueous sodium carbonate solution. After removal of the ether, the residue was benzil (0.7 g., 35%); this melted at 94~95°C alone or with an authentic sample of benzil. The aqueous layer was acidified by 6N-H_2SO_4 and extracted with ether. After removal of the ether, the residue was sublimed to give benzoic acid (1.4 g., 57%), m.p. 121~122°C; its melting point was not depressed on admixing with an authentic sample.

(b) A mixture of benzil (1.0 g., 1/200 mol.) and the copper complex prepared in Experiment 4b was treated as in Experiment 5a. Benzil (0.9 g., 90%) was recovered; m. p. 94~95°C, its melting point was not depressed with an authentic sample. No benzoic acid was obtained.

(c) When diethylamine (10 g., excess) was added to the copper complex prepared in Experiment 4a, the color of the solution did not change. A mixture of benzil (1.0 g., 1/200 mol.) and the resulting copper complex was treated as in Experiment 5a. Benzoic acid (1.1 g., 90%) was obtained; m. p. 121~122°C, its melting point was not depressed on admixing with an authentic sample. No benzil was recovered.

(d) When trimethylamine hydrochloride (3.9g., 3/100 mol.) was added to the copper complex prepared in Experiment 4a, blue needles appeared, and trimethylamine was separated. The mixture of benzil (1.0 g., 1/200 mol.) and the resulting copper complex was treated as in Experiment 5a. Benzil (0.9 g., 90%) was recovered; it melted at 94~95°C alone or with an authentic sample of benzil. No benzoic acid was obtained.

(6) Oxidation of Aniline in the Presence of Methyl Alcohol.—(a) A mixture of aniline (2.0 g., 2.2/100 mol.) and the copper complex described in Experiment 4a [prepared from $CuCl_2 \cdot 2H_2O$ (3.4 g.), KOH (1.1 g.), methyl alcohol (10 cc.) and pyridine (50 cc.)] was treated as in Experiment 1. Azobenzene (0.9 g., 45%) was obtained; it melted at 67~68°C alone or with an authentic sample of azobenzene.

(b) A mixture of aniline (2.0 g., 2.2/100 mol.), cuprous chloride (2.0 g., 1/100 mol.), methyl alcohol (100 cc.) and pyridine (50 cc.) was treated as in Experiment 1. Azobenzene (0.1 g., 5%) was obtained; it melted at 67~68°C alone or with an authentic sample of azobenzene.

(7) Effect of Bases on "Oxidant A".—(a) Cuprous chloride (2.0 g., 1/100 mol.) in pyridine (50 cc.) was oxidized with air at room temperature for 2 hr.

(b) When potassium hydroxide (1.1 g., 2/100 mol.) in methyl alcohol (50 cc.) was added to the copper complex prepared in Experiment 7a, brown precipitate appeared. Its mixture with benzil (1.0 g., 1/200 mol.) was treated as in Experiment 5a. The same results as in Experiment 5b were obtained.

(c) When diethylamine (10 g., excess) was added to the copper complex prepared in Experiment 7a, no color change occurred. A mixture of benzil (1.0 g., 1/200 mol.) and the resulting copper complex, was treated as in Experiment 5a. The same results as in Experiment 5c were obtained.

(d) When trimethylamine hydrochloride (3.9 g., 3/100 mol.) was added to the copper complex prepared in Experiment 7a, blue needles were formed, and trimethylamine was separated. A mixture of benzil (1.0 g., 1/200 mol.) and the resulting copper complex, was treated as in Experiment 5a. The same results as in Experiment 5d were obtained.

Results and Discussion

By aerial oxidation catalyzed by "oxidant A", aniline is converted into azobenzene in a yield of about 60%. Through the treatment of aniline with "oxidant A" in the absence of air, azobenzene and cuprous chloride are obtained (Table I). These results suggest that "oxidant A" is the actual oxidant in the aerial oxidation of aniline catalyzed by cuprous chloride in a pyridine solution. Similar facts were found in the oxidative cleavage of benzil under the similar condition[2].

Table I. Oxidation of Aniline by Cuprous Chloride, Pyridine and Air

Catalyst	Cu_2Cl_2 in the catalyst g. (mol.)	Pyridine cc.	Azobenzene g. (%)
Oxidant A*	8.0 (4/100)	100	0.5**
Cu_2Cl_2	2.0 (2/200)	50	1.2 (60)
Oxidant A	1.0 (1/200)	50	1.2 (60)
Oxidant A	2.0 (2/200)	50	1.2 (60)
Oxidant A	3.0 (3/200)	80	1.2 (60)
Oxidant A	4.0 (4/200)	100	1.2 (60)

Aniline (2.0 g., 2.2/100 mol.) was treated.
* Nitrogen atomosphere.
** Cuprous chloride was obtained.

In the presence of an excess of acidic substance "oxidant A" has no longer its catalytic activity (Table II). The oxidation of benzil is stopped after a definite amount of benzil is oxidized[2], because the produced benzoic acid retards the reaction. On the other hand, "oxidant A" keeps its catalytic activity during the

aerial oxidation of aniline, because acidic substance is hardly produced in the reaction.

TABLE II. EFFECT OF ACIDIC SUBSTANCE

Cu_2Cl_2 g. (mol.)	Acidic substance g. (mol.)	Azobenzene g.
2.0 (1/100)	Acetic acid 1.8 (3/100)	0
2.0 (1/100)	Ammonium chloride 1.6 (3/100)	0
2.0 (1/100)	Trimethylamine hydrochloride* 3.9 (3/100)	0

Aniline (2.0 g., 2.2/100 mol.) was treated in pyridine (100 cc.).
* Trimethylamine was separated.

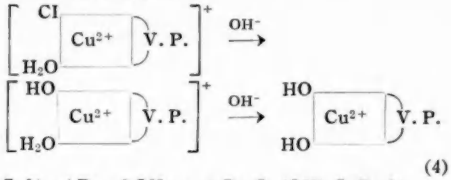
Another catalyst for benzil is obtained from reaction of cupric chloride pyridine complex with a methyl alcohol solution of potassium hydroxide — not with its aqueous solution. With a methyl alcohol solution of potassium hydroxide, cupric chloride pyridine complex—blue needles—turns to a greenish solution, as far as the molar ratio of cupric chloride to potassium hydroxide reaches 1:1.5. Benzil is oxidized to benzoic acid by aerial oxidation catalyzed by this greenish cupric complex—"oxidant B". The amount of oxidized benzil apparently increases in accordance with the amount of added potassium hydroxide (Table III).

TABLE III. OXIDATION OF BENZIL BY "OXIDANT B" AND AIR

$CuCl_2 \cdot 2H_2O$* g. (mol.)	KOH g. (mol.)	Benzoic acid g. (%)	Sample (recovered) g. (%)
3.4 (2/100)	0	0	1.8 (90)
3.4 (2/100)	0.6 (1/100)	0.6 (25)	1.4 (70)
3.4 (2/100)	1.1 (2/100)	1.4 (58)	0.7 (35)
3.4 (2/100)	1.7 (3/100)	2.0 (82)	0.3 (15)

Benzil (2.0 g., 1/100 mol.) was treated.
* Cf. Experiment 4a.

The following change was postulated in the reaction of dichloro-(2-vinyl pyridine)-copper(II) with potassium hydroxide[6] (Reaction 4). It was reported that by reaction of an aqueous cupric salt pyridine complex solution with equimolar potassium hydroxide, a solution of hydroxy cupric salt pyridine complex ion [I] was produced[7] (Reaction 5). All this seems to lead to the conclusion that "oxidant B" is hydroxy cupric chloride pyridine complex.



(4)

$$2\,Cu^{2+} + 4\,Py + 2\,OH^- \rightleftarrows Py_2Cu(OH)_2CuPy_2^{2+} \quad [I] \qquad (5)$$

(V. P.: Vinyl pyridine, Py: Pyridine).

By aerial oxidation catalyzed by "oxidant B", aniline is converted into azobenzene, although the yield of azobenzene is decreased in the presence of an excess of methyl alcohol. The aerial oxidation of aniline catalyzed by "oxidant A" is also retarded by an excess of methyl alcohol (Table IV).

TABLE IV. EFFECT OF METHYL ALCOHOL ON THE AERIAL OXIDATION OF ANILINE

Copper salt in the catalyst* g. (mol.)		KOH in the catalyst g. (mol.)	Methyl alcohol cc.	Azobenzene g. (%)
Cu_2Cl_2	2.0 (1/100)	0	100	0.1 (5)
	3.4 (2/100)	0	20	0
$CuCl_2 \cdot 2H_2O$	3.4 (2/100)	1.1 (2/100)	100	0
	3.4 (2/100)	1.1 (2/100)	20	0.3 (15)
	3.4 (2/100)	1.1 (2/100)	10	0.9 (45)

Aniline (2.0 g., 2.2/100 mol.) was treated.
* Pyridine (50 cc.) was used as a solvent.

When equimolar potassium hydroxide in methyl alcohol is added "oxidant A" or "oxidant B", these complexes are destroyed and their catalytic activity is lost. However, when "oxidant A" or "oxidant B" is treated with excessive diethylamine or benzylamine, they keep their color and their catalytic activity. Through the reaction between trimethylamine hydrochloride and "oxidant A" or "oxidant B", trimethylamine separates. The resulting complexes no longer have their catalytic activity. This fact suggests that "oxidant A" and "oxidant B" have stronger basicity than trimethylamine (Ref. 7).

All the phenomena described above suggest that there is a remarkable resemblance between "oxidant A" and "oxidant B".

Summary

(1) By aerial oxidation of aniline catalyzed by cuprous chloride in a pyridine solution, azobenzene of about 60% is

6) J. F. Pudivin et al., *J. Am. Chem. Soc.*, **78**, 2104 (1956).
7) D. L. Leussing et al., ibid., **79**, 4270 (1957).

produced. In this reaction, the actual oxidant may be considered "oxidant A" which is produced by aerial oxidation of cuprous chloride pyridine complex.

(2) Hydroxy cupric chloride pyridine complex, a reaction product of cupric chloride pyridine complex with a methyl alcohol solution of potassium hydroxide, has a similar catalytic activity.

(3) These two complexes are to be considered strong bases.

(4) These two complexes have a remarkable resemblance to each other.

The author wishes to express his sincere gratitude to Professor Ryozo Goto for his invaluable advice and unfailing encouragement of this work.

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*On the Mechanism of Oxidation by Cuprous Chloride, Pyridine and Air. II. The Mechanism of Formation of Azobenzene from Aniline**

By Keizō KINOSHITA

(Received September 30, 1958)

Terent'ev et al.[1] reported that when aerial oxidation of aniline was carried out in a pyridine solution catalyzed by cuprous chloride, azobenzene was obtained in a good yield. In Part I of this series, the details of this reaction were studied and it was considered that the actual oxidant of this oxidation was "oxidant A" obtained by aerial oxidation of cuprous chloride pyridine complex[2]. In this paper, the mechanism of this reaction is discussed.

Experimental

Materials.—Aniline (b. p. 184~185°C), *o*-toluidine (b. p. 199~200°C) and *o*-anisidine (b. p. 225°C) were redistilled immediately before use. Extra chemical pure grade *p*-toluidine (m. p. 44~45°C) and *p*-anisidine (m. p. 56~57°C) were used. Cuprous acetate pyridine complex was prepared as follows. When cupric acetate (3.8 g., 2/100 mol.) in pyridine (50 cc.) was refluxed for 2 hr., deep blue crystals were formed (cupric acetate pyridine complex). A mixture of metallic copper (0.5 g. excess) and the above pyridine solution of cupric acetate pyridine complex was stirred at 60°C in a stream of nitrogen until the color of the solution was turned to dark yellow.

(1) Attempted Aerial Oxidation of Aniline Catalyzed by the Copper Acetate Complexes.—(a) A mixture of aniline (2.0 g., 2.2/100 mol.) and the above-mentioned cuprous acetate pyridine complex in pyridine was stirred for 5 hr. at 30°C in a stream of air. The resulting mixture was acidified with 6N-H_2SO_4, and extracted with ether (500 cc.). After removal of the ether, a trace of residue was obtained. The residue was dissolved with light petroleum (b. p. 40~60°C) and chromatographed on activated alumina (Wako Pure Chemical Industries, Ltd.). All the substance remained on top of the activated alumina. No azobenzene was obtained. The color of the aqueous layer was blue.

(b) Potassium hydroxide (1.1 g., 2/100 mol.) in methyl alcohol (10 cc.) was added to a cupric acetate pyridine complex in pyridine (described in the preparation of cuprous acetate pyridine complex). A mixture of aniline (2.0g., 2.2/100 mol.) and the resulting copper complex was stirred at 80°C for 5 hr. in a stream of air. The resulting mixture was treated as in Experiment 1a. The same results as in Experiment 1a were obtained.

(2) Oxidation of Substituted Anilines.—(a) A mixture of *p*-toluidine (2.2 g., 2/100 mol.), cuprous chloride (2.0 g., 1/100 mol.) and pyridine (50 cc.) was stirred for 5 hr. at room temperature in a stream of air. The resulting mixture was acidified with 6N-H_2SO_4, and extracted with ether (500 cc.). After removal of the ether, the residue was dissolved with benzene, and chromatographed on activated alumina. 4,4'azotoluene (2.0 g., 90%) was obtained; m. p. 142~143°C (Lit. 143°C). It was identified with 4,4'azotoluene by a mixed melting point determination and an analysis.

Anal. Found: C, 80.10; H, 6.92; N, 13.16.

* The present work was presented at the Symposium on the Mechanism of Organic Chemical Reaction of the Chemical Society of Japan, held at Nagoya in October, 1957.

1) A. P. Terent'ev et al., *Doklady Akad. Nauk, U. S. S. R.*, **1955**, 91—93. [*Chem. Abstr.*, **50**, 4807 (1956).]

2) K. Kinoshita, Part I of this series in This Bulletin, **32**, 777 (1959).

Calcd. for $C_{14}H_{14}N_2$: C, 80.00; H, 6.66; N, 13.33%.

A trace of black substance remained on top of the activated alumina.

(b) A mixture of *p*-anisidine (2.5 g., 2/100 mol.), cuprous chloride (2.0 g., 1/100 mol.) and pyridine (50 cc.) was treated as in Experiment 2a. 4,4'Azoanisol (2.2 g., 88%) was obtained; m. p. 162~163°C (Lit. 163°C). It was identified with 4,4'azoanisol by a mixed melting point determination and an analysis.

Anal. Found: C, 69.54; H, 5.96; N, 11.47. Calcd. for $C_{14}H_{14}O_2N_2$: C, 69.42; H, 5.78; N, 11.57%.

A trace of black substance remained on top of the activated alumina.

(c) A mixture of *o*-toluidine (2.2 g., 2/100 mol.), cuprous chloride (2.0 g., 1/100 mol.) and pyridine (50 cc.) was treated as in Experiment 2a. The resulting mixture was acidified with 6N-H_2SO_4, and extracted with ether (500 cc.). After removal of the ether, the residue was distilled with steam; then a large amount of substance remained in the vessel. From the distillate 2,2'-azotoluene (0.3 g., 14%) was obtained; m. p. 54~55°C (Lit. 55°C). It was identified with 2,2'-azotoluene by a mixed melting point determination and an analysis.

Anal. Found: C, 79.93; H, 6.89; N, 13.19. Calcd. for $C_{14}H_{14}N_2$: C, 80.00; H, 6.66; N, 13.33%.

The aqueous layer was dark violet.

(d) A mixture of *o*-anisidine (2.5 g., 2/100 mol.), cuprous chloride (2.0 g., 1/100 mol.) and pyridine (50 cc.) was treated as in Experiment 2a. 2,2'-Azoanisol (0.4 g., 16%) was obtained; m. p. 153~154°C (Lit. 153°C). It was identified with 2,2'-azoanisol by a mixed melting point determination and an analysis.

Anal. Found: C, 69.41; H, 5.98; N, 11.44. Calcd. for $C_{14}H_{14}O_2N_2$: C, 69.42; H, 5.78; N, 11.57%.

A large amount of substance remained on the activated alumina. There were some substances which did not dissolve in ether. The color of the aqueous layer was dark violet.

(3) Oxidation of Hydrazobenzene.—Cuprous chloride (2.0 g., 1/100 mol.) in pyridine (50 cc.) was oxidized with air for 2 hr. at room temperature. When hydrazobenzene (2.0 g., 1.1/100 mol.) was added to the resulting copper complex, the color of the solution was turned to yellow. The yellow solution was stirred for 1 hr. at room temperature in a stream of air. From the resulting mixture azobenzene (1.9 g., 95%) was obtained; melted at 67~68°C alone or with an authentic sample of azobenzene.

(4) Competitive Oxidation of Aniline and *p*-Anisidine.—A mixture of aniline (3.6 g., 4/100 mol.), *p*-anisidine (5.0 g., 4/100 ml.), cuprous chloride (1.0 g., 1/200 mol.) and pyridine (50 cc.) was stirred at room temperature in a stream of air. The resulting mixture was acidified with 6N-H_2SO_4 and filtered. The residue was continuously extracted for 24 hr. with light petroleum (b. p. 40~60°C, 100 cc.). A trace of black substance remained. From the extract 4,4'azoanisol was separated; this melted at 163~164°C alone or with an authentic sample of 4,4'azoanisol. When the reaction was carried out for 30 min. and 60 min., the obtained 4,4'azoanisol amounted to 1.2 g. and 2.3 g. respectively, and the residues, after removal of the mother liquor, were 0.1 g. and 0.2 g., respectively.

Results and Discussion

Since it was reported that the chlorine ion in cupric chloride complexes was easily substituted[3], chlorine ion in "oxidant A" I may also be substituted by aniline or methyl alcohol (Reactions 1 and 2). On the other hand, acetate ion in cupric acetate complexes may not be substituted easily by the above compounds (Ref. 3).

$$\underset{\text{I}}{C_6H_5NH_2} + \underset{\text{I}}{Cu(II)\text{-}Cl} \rightleftarrows \underset{\text{II}}{[C_6H_5NH_2Cu(II)]^+Cl^-} \quad (1)$$

$$CH_3OH + Cu(II)\text{-}Cl \rightleftarrows [CH_3OH\text{-}Cu(II)]^+Cl^- \quad (2)$$

An excess of methyl alcohol retards the aerial oxidation of aniline[2]—it may be caused by a competition between Reactions 1 and 2. Cuprous acetate pyridine complex or hydroxy cupric acetate pyridine complex has no catalytic activity to the aerial oxidation of aniline (Table I). From these facts II may be considered as an intermediate in this reaction.

Table I. Catalytic activity of copper acetate complex

Pyridine complex* of copper salts	Temp. °C	Azobenzene g.(%)
Cuprous chloride**	25	1.5(75)
Cuprous acetate	30	0
Cuprous acetate	60	0
Cuprous acetate	80	0
Hydroxy cupric acetate	80	0

Aniline (2.0 g., 2.2/100 mol.) was treated for 5 hr.

* Cf. Experiment 1.

** Cupric chloride pyridine complex was reduced by metallic copper.

Syrkin et al. reported that in ammino complexes, the basic properties of the nitrogen atom were reduced, but that the acidic properties correspondingly increased[4]. By the reaction between II and I which is considered to be a strong base[2], a proton is removed from II to form an intermediate III.

3) H. Taube, *Chem. Revs.*, **50**, 69 (1952).

4) Y. K. Syrkin et al., "Structure of Molecules and the Chemical Bond", Interscience Publisher, New York (1950), p. 387.

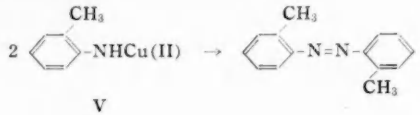
$$[\underset{II}{Cu(II)\text{-}NH_2C_6H_5}]^+Cl^- \rightarrow \underset{I}{Cu(II)\text{-}Cl} + \underset{III}{NHC_6H_5} \quad (3)$$

By aerial oxidation of an equimolar mixture of aniline and *p*-anisidine catalyzed by a small amount of cuprous chloride, 4,4'azoanisol is selectively obtained in the early stage of this reaction (Experiment 4). This result suggests that IV reacts with another IV to produce 4,4'azoanisol (Reaction 4), because the reaction between IV and free amines, may accompany 4-methoxy azobenzene with 4,4'azoanisol, even in the early stage of this reaction.

$$2\ (p\text{-})CH_3OC_6H_4NH\text{-}Cu(II) \quad (IV)$$
$$\rightarrow (p\text{-})CH_3OC_6H_4N=NC_6H_4OCH_3(p\text{-}) \quad (4)$$

By aerial oxidation catalyzed by cuprous chloride in a pyridine solution, *p*-toluidine and *p*-anisidine are converted into the corresponding azo compounds almost quantitatively, while *o*-toluidine and *o*-anisidine are converted into the corresponding azo compounds only in a poor yield, although many other products are formed besides the azo compounds (Table II).

It was reported that the yield of azo compounds from substituted anilines were hardly affected at all by the position of the substituents in these amines, if these azo compounds were produced from the dimerisation of intermediate free radicals[5,6]. On the other hand, the steric hindrance of ortho substituent in V may interfere with the approach of two nitrogen atoms to decrease the yield of 2,2'-azotoluene,



(5)

if 2,2'azotoluene is produced from a reaction of V with another V, (Reaction 5). The experimental results prove this to be valid.

Hydrazobenzene is converted into azobenzene almost quantitatively, by aerial oxidation catalyzed by "oxidant A" in a pyridine solution (Experiment 3). Accordingly, it is reasonable to assume that III is converted primarily into hydrazobenzene, which is further oxidized to azobenzene[5,6].

$$2\ \underset{III}{C_6H_5NH\text{-}Cu(II)} \rightarrow C_6H_5NH\text{-}NHC_6H_5 \rightarrow C_6H_5N=NC_6H_5 \quad (6)$$

In a pyridine solution, it was reported that cuprous salts and complexes increased in their stability[7]. Consequently, the activated complex may be as VI[8]. By the reaction of VI with another VI, hydrazobenzene and cuprous complex are produced. Hydrazobenzene is further oxidized to azobenzen (Reaction 7).

$$\underset{III}{C_6H_5NH\text{-}Cu(II)} \rightleftarrows [\underset{VI}{Cu(I)\text{-}\dot{N}HC_6H_5}]$$
$$2\ [Cu(I)\text{-}\dot{N}HC_6H_5] \rightarrow C_6H_5NH\text{-}NHC_6H_5 + 2\ Cu(I)$$
$$C_6H_5NH\text{-}NHC_6H_5 \rightarrow C_6H_5N=NC_6H_5 \quad (7)$$

TABLE II. OXIDATION OF SUBSTITUTED ANILINES

Amine g.(mol.)	Cu_2Cl_2 g.(mol.)	Time (hr.)	Azocompound g. (%)
p-Toluidine 2.2(2/100)	2.0(1/100)	5	4,4'Azotoluene 2.0 (90)
p-Anisidine 2.5(2/100)	2.0(1/100)	5	4,4'Azoanisol 2.2 (88)
o-Toluidine 2.2(2/100)	2.0(1/100)	5	2,2'Azotoluene 0.3 (14)
o-Toluidine 4.4(4/100)	4.0(2/100)	6	2,2'Azotoluene 0.8 (18)
o-Toluidine 8.8(8/100)	8.0(4/100)	8	2,2'Azotoluene 1.7 (20)
o-Anisidine 2.5(2/100)	2.0(1/100)	5	2,2'Azoanisol 0.4 (16)
p-Toluidine 1.1(1/100)	2.0(1/100)*	5	4,4'Azotoluene** 0.5
o-Anisidine 2.5(2/100)	4.0(2/100)*	20	2,2'Azoanisol** 0.2

* "Oxidant A" was used.
** Absence of air.

Summary

(1) Attempted aerial oxidation of aniline, catalyzed by cuprous acetate pyridine complex, is unsuccessful even at 80°C.

(2) By the aerial oxidation of equimolar mixture of aniline and *p*-anisidine, catalyzed by a small amount of cuprous chloride, 4,4'azoanisol is selectively obtained in the early stage of this reaction.

(3) By the aerial oxidation catalyzed by cuprous chloride in a pyridine solution, the yields of the azo compounds, which are produced from *p*-toluidine and *p*-anisidine, are almost quantitative. On

5) K. H. Pausacker, *J. Chem. Soc.*, **1953**, 1989.
6) K. H. Pausacker et al., ibid., **1954**, 4003.
7) J. E. B. Landles, ibid., **1942**, 802.
8) R. E. Connick, *J. Phys. Chem.*, **56**, 21 (1952). In this remark, he described the activated complex in which oxidized cyanide ion was combined with $[Cu(CN)_3]^{2-}$ in the oxidation of cyanide ion with cupric ion.

the other hand, the yields of the azo compounds, which are produced from *o*-toluidine and *o*-anisidine, are very poor.

(4) In this reaction, it is postulated that an intermediate [Cu(II)–NHC_6H_5] is initially formed, and that hydrazobenzene and cuprous complex are produced by the bimolecular reaction of this intermediate.

(5) Hydrazobenzene is converted into azobenzene almost quantitatively under the same condition as aniline is oxidized.

The author wishes to express his sincere gratitude to Professor Ryozo Goto for his invaluable advice and unfailing encouragement of this work.

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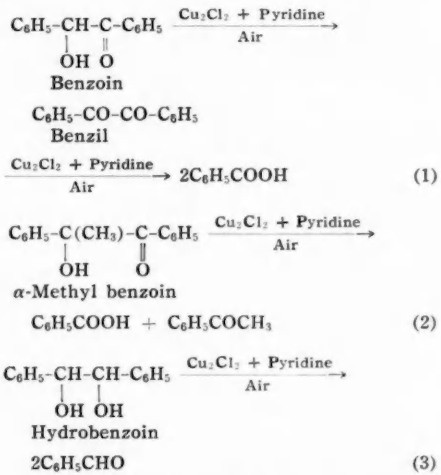
*On the Mechanism of Oxidation by Cuprous Chloride, Pyridine and Air. III. On the Mechanism of Oxidative Cleavage of Benzil, α-Methyl Benzoin and Hydrobenzoin**

By Keizō KINOSHITA

(Received September 30, 1958)

An earlier work reported that by aerial oxidation catalyzed by cuprous chloride in a pyridine solution, benzoin, benzil, α-methyl benzoin and hydrobenzoin were oxidized to break down as follows[1].



It was also discovered that in these reactions, the actual oxidant was "oxidant A" which was produced by aerial oxidation of cuprous chloride pyridine complex[2]. In this paper, the mechanism of oxidative cleavage of the above compounds is discussed.

Experimental

Materials.—Benzil was prepared by oxidation of benzoin with nitric acid, and recrystallized from alcohol, m.p. 94~95°C[4]. α-Methyl benzoin was prepared by reaction of benzil with methyl magnesium iodide, and recrystallized from ligroin (b.p. 80~100°C), m.p. 90~91°C[5]. Hydrobenzoin was prepared by reduction of benzoin with aluminum *iso*-propylate, and recrystallized from aqueous alcohol, m.p. 135~136°C[6].

(1) Preparation of Catalysts.—(a) "Oxidant A": Cuprous chloride (4.0 g., 2/100 mol.) in pyridine (50 cc.) was oxidized with air for 2 hr. at room temperature.

(b) "Oxidant B": Potassium hydroxide (2.2 g., 4/100 mol.) in methyl alcohol (50 cc.) was added with stirring to cupric chloride pyridine complex (prepared from $CuCl_2 \cdot 2H_2O$ (6.8 g., 4/100 mol.) and pyridine (50 cc.)).

(c) "Oxidant C": Cuprous acetate pyridine complex[3] (prepared from $Cu(OAc)_2 \cdot H_2O$ (3.8 g., 2/100 mol.) and pyridine (50 cc.)), was oxidized with air for 2 hr. at room temperature.

(d) "Oxidant D": Potassium hydroxide

* The present work was presented at the Symposium on the Mechanism of Organic Chemical Reaction of the Chemical Society of Japan, held at Sendai in October, 1956.

1) K. Kinoshita, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **75**, 48 (1954).

2) K. Kinoshita, ibid., **75**, 175 (1954).

3) K. Kinoshita, Part II of this series in This Bulletin, **32**, 780 (1952).

4) R. Adams, "Organic Synthesis", Vol. I, John Wiley & Sons, Inc., New York (1921), p. 25.

5) R. Nodzu et al., *J. Chem. Soc. Japan* (*Nippon Kagaku Kaishi*), **59**, 1237 (1938).

6) H. Lunde, *Ber.*, **70**, 1520 (1937).

(2.2 g., 4/100 mol.) in methyl alcohol (50 cc.) was added with stirring to cupric acetate pyridine complex (prepared from $Cu(OAc)_2 \cdot H_2O$, (7.6 g., 4/100 mol.) and pyridine (50 cc.)).

(2) Oxidation of Benzil.—(a) When methyl alcohol (50 cc.) was added to "oxidant A", the color of the solution turned to green. A mixture of benzil (2.0 g., 1/100 mol.) and the greenish solution was stirred at 30°C for 2 hr. in a stream of air. The resulting mixture was acidified with 6N-H_2SO_4, and extracted with ether (500 cc.). The ethereal layer was washed with water and extracted with aqueous sodium carbonate solution. After removal of the ether, a trace of the substance remained. The sodium carbonate solution was acidified with 6N-H_2SO_4, and extracted with ether (500 cc.). After removal of the ether, the residue was sublimed to give benzoic acid (2.1 g., 86%); it melted at 121~122°C alone or with an authentic sample of benzoic acid.

The same results were obtained with "oxidant C" or "oxidant D" in place of "oxidant A".

(b) When trimethylamine hydrochloride (7.8 g., 6/100 mol.) was added to "oxidant C or D", trimethylamine was separated, and dark blue needles appeared. The mixture of benzil (2.0 g., 1/100 mol.) and the resulting complex was treated as above. No benzoic acid was obtained. Benzil 1.8 g., 90%) was recovered; it melted at 94~95°C alone or with an authentic sample of benzil.

(3) Oxidation of Hydrobenzoin.—(a) A mixture of hydrobenzoin (2.0 g., 1/100 mol.), methyl alcohol (10 cc.) and "oxidant A" (prepared from Cu_2Cl_2 (2.0 g., 1/100 mol.)) was stirred at 30°C for 4 hr. in a stream of air. The resulting mixture was acidified with 6N-H_2SO_4, and extracted with ether (500 cc.). The ethereal layer was washed with water, and extracted with aqueous sodium carbonate solution. After removal of the ether, the residue was treated with aqueous sodium hydrogen sulfite solution. The mixture was filtered. The precipitate was washed with water and dried. Hydrobenzoin (1.3 g., 65%) was recovered; m.p. 135~136°C, its melting point was not depressed on admixing with an authentic sample. From the sodium hydrogen sulfite solution, benzaldehyde phenyl hydrazone (0.8 g., 20%) was obtained; m.p. 155~156°C (Lit. 156°C). It was identified with benzaldehyde phenyl hydrazone by a mixed melting point determination and an analysis.

Anal. Found: C, 79.36; H, 6.38; N, 14.32. Calcd. for $C_{13}H_{12}N_2$: C, 79.59; H, 6.12; N, 14.28%.

From the sodium carbonate solution, a trace of benzoic acid was obtained. It was identified by converting it into salicylic acid[7].

(b) A mixture of hydrobenzoin (2.0 g., 1/100 mol.) and "oxidant C or D" was stirred for 4 hr. in a stream of air. Although the oxidation was attempted at 30, 60 and 80°C, no oxidation products were obtained, and hydrobenzoin (1.8 g., 90%) was recovered; it melted at 135~136°C alone or with an authentic sample of hydrobenzoin.

(4) Reaction of Cupric Chloride with Hydrobenzoin in the Presence of Potassium Hydroxide. — When cupric chloride (1.7 g., 1/100 mol.) in methyl alcohol (20 cc.) was added to a mixture of hydrobenzoin (4.0 g., 2/100 mol.), potassium hydroxide (2.8 g., 5/100 mol.), pyridine (20 cc.) and methyl alcohol (20 cc.), a deep blue solution was formed. When ethylene glycol was used in place of hydrobenzoin, a similar result was obtained. But in the absence of such glycols, brown precipitate appeared. Even after this deep blue solution was kept for 24 hr. room temperature, cuprous oxide did not appear.

(5) Oxidation of α-Methyl Benzoin.—(a) A mixture of α-methyl benzoin (2.0 g., 0.8/100 mol.), "oxidant A" and methyl alcohol (50 cc.) was stirred at 30°C for 4 hr. in a stream of air. The resulting mixture was acidified with 6N-H_2SO_4, and extracted with ether (500 cc.). The ethereal layer was washed with water, and extracted with aqueous sodium carbonate solution. After removal of the ether, the residue was treated with aqueous semicarbazide hydrochloride and sodium acetate solution. The resulting mixture was filtered and washed with benzene. The residue was pure acetophenone semicarbazone (0.6 g., 40%); m. p. 197~198°C (Lit. 198°C). It was indentified with acetophenone semicarbazone by a mixed melting point determination and an analysis.

Anal. Found: C, 61.15; H, 6.52; N, 23.72. Calcd. for $C_9H_{11}ON_3$: C, 61.00; H, 6.25; N, 23.72%.

After removal of the benzene, the residue was recrystallized from ligroin (b. p. 80~100°C). α-Methyl benzoin (0.7 g., 35%) was recovered; m.p. 90~91°C, its melting point was not depressed on admixing with an authentic sample. From the sodium carbonate solution, benzoic acid (0.5 g., 50%) was obtained; it melted at 121~122°C alone or with an authentic sample of benzoic acid.

(b) A mixture of α-methyl benzoin (2.0 g., 0.8/100 mol.) and "oxidant C or D", was stirred for 4 hr. in a stream of air. Although the oxidation was attempted at 30, 60 and 80°C, no oxidation products were obtained, and α-methyl benzoin (1.7 g., 85%) was recovered, m.p. 90~91°C; its melting point was not depressed on admixing with an anthentic sample.

Results and Discussion

Cuprous acetate pyridine complex has a similar catalytic activity as cuprous chloride pyridine complex for aerial oxidation of benzil. Hydroxy cupric acetate pyridine complex (Experiment 1d) has a similar activity as cuprous acetate pyridine complex for these reactions (Experiment 2a). Furthermore, the oxidation of benzil is hardly retarded at all by an excess of methyl alcohol (Table I).

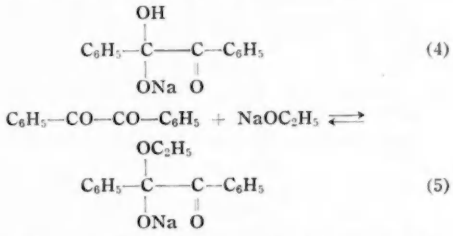
7) H. Meyer, "Nachweis und Bestimmung Organischer Verbindungen", Julius Springer, Wien (1933), p. 314.

TABLE I. EFFECT OF METHYL ALCOHOL ON THE OXIDATION OF BENZIL

Catalyst	Copper salt in the catalyst		Methyl alcohol	Benzoic acid
		g.	cc.	g. (%)
Oxidant A*	Cu_2Cl_2,	4.0	50	2.1 (86)
Oxidant A*	Cu_2Cl_2,	4.0	100	2.1 (86)
Oxidant B*	$CuCl_2 \cdot 2H_2O$,	6.8	50	2.0 (82)
Oxidant B*	$CuCl_2 \cdot 2H_2O$,	6.8	100	2.0 (82)

Benzil (2.0 g.) was treated.
* Cf. Experiment 1.

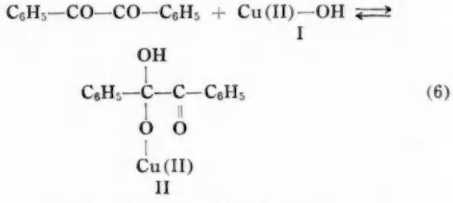
It was reported that strong bases were capable of combining to the keto group of benzil in alcohol[5,8]. (Reactions 4 and 5).



(4)

(5)

"Oxidant A, B, C** and D**" are belived to be strong bases[9]. Since "oxidant B". I is considered to have hydroxy group[9], it can also combine with benzil at its keto group to form II —— this addition reaction seems not to be easily retarded with an excess of methyl alcohol. Since "oxidant A" and "oxidant B" bear a remarkable resemblance, a similar intermediate may be produced by reaction of benzil with "oxidant A".



(6)

An attempt to oxidize hydrobenzoin by aerial oxidation catalyzed by "oxidant C" or "oxidant D" is unsuccessful even at 80°C. (Experiment 3b), although it is oxidized to benzaldehyde by aerial oxidation catalyzed by "oxidant A" or "oxidant B". Furthermore, an excess of methyl alcohol retards the oxidation (Table II).

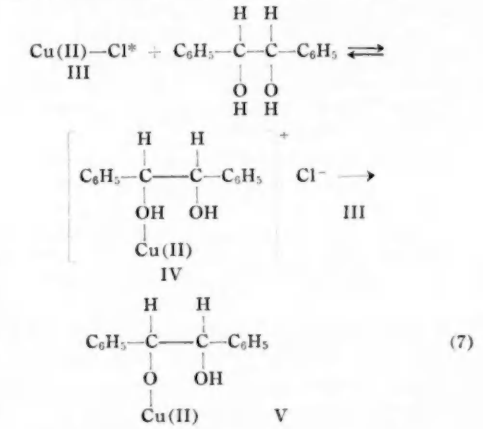
8) A. Lachmann, *J. Am. Chem. Soc.*, **45**, 1509 (1923).
** Cf. Experiment 1.
9) K. Kinoshita, Part I of this series in This Bulletin, **32**, 777 (1959).

TABLE II. EFFECT OF METHYL ALCOHOL ON THE OXIDATION OF HYDROBENZOIN

Catalyst	Methyl alcohol	Benz-aldehyde	Benzoic acid	Sample (Recovered)
	cc.	g. (%)	g. (%)	g. (%)
Oxidant A*	0	1.0 (50)	0.1 (4)	0.6 (30)
Oxidant A*	10	0.4 (20)	trace	1.3 (65)
Oxidant A*	50	0.2 (10)	trace	1.5 (75)
Oxidant B**	10	0.5 (25)	trace	1.1 (55)
Oxidant B**	50	trace	trace	1.7 (85)

Hydrobenzoin (2.0 g.) was treated.
* Cu_2Cl_2, 2.0 g. ** $CuCl_2 \cdot 2H_2O$, 1.7 g.

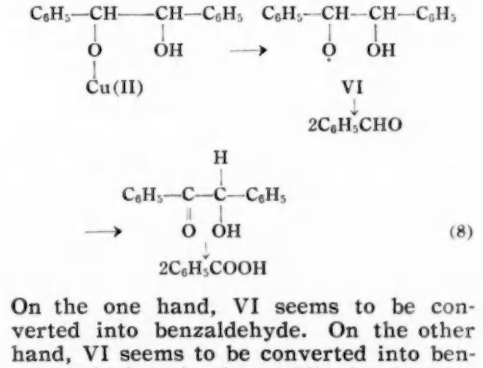
These results are similar to those obtained in the aerial oxidation of aniline[3]. Thus a similar intermediate to that postulated in the oxidation of aniline, may be produced (Reaction 7) (Ref. 3).



(7)

* Cu(II)-Cl stands for "oxidant A".

If V is converted directly into benzaldehyde, a free racidal such as VI would appear in this reaction.



(8)

On the one hand, VI seems to be converted into benzaldehyde. On the other hand, VI seems to be converted into benzoin, which is further oxidized to benzoic acid. Thus, if VI appears in this reaction, a good amount of benzoic acid may be

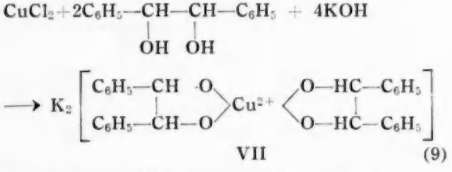
obtained. Since this assumption is not supported by the experimental results[1], it is postulated that such a free radical as VI hardly ever appears in this reaction. Moreover, if VI were intermediate, the stability of benzyl alcohol to "oxidant A" (Ref. 2) would be inexplicable.

Deep blue color is developed upon the addition of cupric chloride—methyl alcohol solution—to a mixture of hydrobenzoin and potassium hydroxide—pyridine-methyl alcohol solution (Experiment 4). For the following reason (1—3), this complex seems to be a chelate compound such as VII.

(1) In the absence of hydrobenzoin, this complex is never formed.

(2) In the presence of ethylene glycol in place of hydrobenzoin, a similar complex is formed.

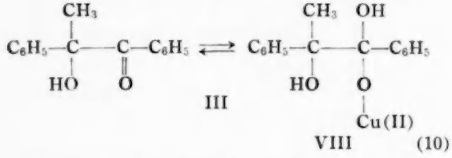
(3) It was reported that *bis*-glycolatocopper(II) complex was produced upon the addition of cupric nitrate to aqueous erythritol anhydride solution in the presence of sodium hydroxide[10].



VII (9)

Cuprous oxide does not appear even after 24 hr. from this deep blue solution and the formation of chelate compounds such as VII seems to have no effect upon the oxidation of hydrobenzoin.

Because strong bases can combine with the keto group of α-methyl benzoin in alcohol[5,11], an intermediate VIII may be produced by the reaction of α-methyl benzoin with "oxidant A" (Reaction 10).



III VIII (10)

However, α-methyl benzoin is not oxidized in aerial oxidation catalyzed by "oxidant C" or "oxidant D" (Experiment 5b). Furthermore, the oxidation of α-methyl benzoin is retarded by an excess of methyl alcohol (Table III).

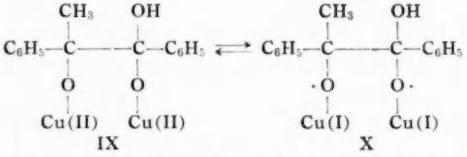
Table III. Effect of methyl alcohol on oxidation of α-methyl benzoin

Catalyst	Methyl alcohol	Benzoic acid	Aceto-phenone	Sample (Recovered)
	cc.	g. (%)	g. (%)	g. (%)
Oxidant A*	0	0.8 (80)	0.8 (80)	0.1 (5)
Oxidant A*	50	0.5 (50)	0.4 (40)	0.7 (35)
Oxidant A*	100	0.2 (20)	0.2 (20)	1.3 (65)
Oxidant B**	50	0.5 (50)	0.5 (50)	0.6 (30)
Oxidant B**	100	trace	trace	1.7 (85)

α-Methyl benzoin (2.0 g.) was treated.
* Cu_2Cl_2, 4.0 g. ** $CuCl_2 \cdot 2H_2O$, 6.8 g.

These results suggest that the hydroxy group of α-methyl benzoin in VIII must be combined with "oxidant A" to form IX.

The oxidative cleavage of IX probably takes place through activated complex X (Ref. 3). As two unpaired electrons are located on both oxygen atoms of α-methyl benzoin respectively in X, it causes a cleavage of α-methyl benzoin (Reaction 11)***.



IX X

$\longrightarrow C_6H_5COCH_3 + C_6H_5COOH + 2Cu(I)$ (11)

Benzil or hydrobenzoin may be oxidized under the same mechanism as described above.

In Part II, the mechanism of the formation of azobenzene in aerial oxidation of aniline catalyzed by cuprous chloride, was discussed[3]. It is believed that the copper-nitrogen linkage in oxidative dimerisation of aniline, is similarly situated to the copper-oxygen linkage in oxidative cleavage of α-methyl benzoin. Thus, the oxidative dimerisation of aniline and oxidative cleavage of α-methyl benzoin, are carried out through similar mechanism.

Summary

(1) Benzil is oxidized by aerial oxidation catalyzed by "oxidants A, B, C and D".

(2) α-Methyl benzoin or hydrobenzoin is oxidized by aerial oxidation catalyzed by "oxidants A and B" only. This reac-

10) H. B. Jonassen et al., *J. Am. Chem. Soc.*, **77**, 2667 (1955). Ref. L. Segal et al., ibid., **78**, 273 (1955); N. V. Sidgwick, "The Chemical Elements and their Compounds", Vol. I, Oxford University Press, London (1950), p. 171; W. Traube et al., *Ber.*, **69**, 2655 (1936).

11) D. B. Sharp et al., *J. Am. Chem. Soc.*, **74**, 5643 (1952).

*** Bawn et al. reported that the biradical with the structure ·CH-CH_2-CH_2-CH· has a strong tendency to break up the linkage between C(2) and C(3); E. H. Bawn et al., *Trans. Faraday Soc.*, **35**, 889 (1939).

tion is retarded by methyl alcohol.

(3) The mechanism of oxidative cleavage of benzil, α-methyl benzoin and hydrobenzoin, is described. It is also considered that the oxidative cleavage of benzil, α-methyl benzoin and hydrobenzoin, and the oxidative dimerisation of aniline[3] are carried out through similar mechanism.

The author wishes to express his sincere gratitude to Professor Ryozo Goto for his invaluable advice and unfailing encouragement of this work.

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Mild Oxidation of Alicyclic Secondary Amines. I. On Formation of Isonitrone from Perhydroquinoline Series

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(Received October 28, 1958)

In recent years, a few papers concerning the nitrones of alicyclic secondary amines, especially piperidine[1,2] and pyrrolidine[3], have been reported. But the obtaining of isonitrone from alicyclic scondary amine has not yet been described. This paper reports on some of the isonitrones obtained from polycyclic compounds in the alicyclic secondary amine series.

Oxidation of *trans*-decahydroquinoline (I) with silver oxide in 30%-methanol solution at a temperature of 30~40°C gave a product, $C_9H_{15}ON$*, m.p. 280~282°C (IV). This product is different from a compound obtained by Witkop[5] from an air oxidation of I. Also from *cis*-decahydroquinoline (II), the same compound IV was obtained under the same condition. This compound was moreover formed by the treatment of I and II with 30%-hydrogen peroxide, perbenzoic acid, or with *N*-bromosuccinimide (NBS) although accompanied by the known hydroperoxide (XIV)[6].

This new substance (IV) was easily soluble in a polar solvent, but not in a non-polar one. In the infrared spectrum (in Nujol) of IV, the NH-stretching band at 2.96 μ which had been observed in that of *trans*-decahydroquinoline (I), disappeared. This compound IV had no unsaturated nature** and did not react with phenylisocyanate. It was reduced with sodium borohydride, sulfurous acid or with acidic potassium iodide, giving I in all cases.

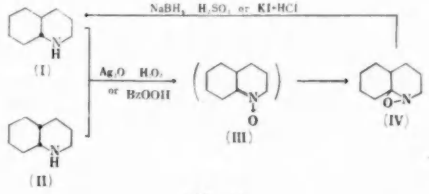


Fig. 1

When α-perhydroacridine (*trans-syn-trans*) (V)[7] was treated with 30%-hydroperoxide at room temperature for a week, it gave a crystalline product, $C_{13}H_{21}ON$*, (sublimed with decomposition at near 320°C) (VI). On the other hand, α-perhydrophenanthridine (*trans-anti-trans*) (VII)[8] reacted with silver oxide at a temperature of 90~100°C, producing a new

1) J. Thesing and H. Mayer, *Ber.*, **89**, 2159 (1956).
2) J. Thesing and H. Mayer, *Ann.*, **609**, 46 (1957).
3) R. F. C. Brown, V. M. Clark and Sir A. Todd, *Proc. Chem. Soc.*, **1957**, 97.
* It is well known that aromatic amine oxides do not appear to form definite hydrates[4a]. Henry and Leete[4b] have recently reported that gramine oxide has hydrogen peroxide of crystallization which is determined by iodometry. These new compounds, IV, VI and VIII, had hydrogen peroxide determined by the same method (described in experimental part).
4a) T. W. J. Taylor and W. Baker, "The Organic Chemistry of Nitrogen by Sidgwick", Oxford University Press, London (1937), p. 167.
4b) D. W. Henry and E. Leete, *J. Am. Chem. Soc.*, **79**, 5254 (1957).
5) B. Witkop, *Experientia*, **10**, 419 (1954).
6) L. A. Cohen and B. Witkop, *J. Am. Chem. Soc.*, **77**, 6575 (1955).
** The compound IV gave a negative test to bromine or tetranitromethane and decolorized only permanganate.
7) T. Masamune and S. Wakamatsu, *J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zasshi)*, **77**, 1145 (1956); *J. Fac. Sci. Hokkaido Univ. Ser. III. Chem.*, **5**, 47 (1957).
8) T. Masamune and Y. Kubota, *J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zasshi)*, **77**, 1468 (1956).

substance, $C_{13}H_{21}ON$*, (sublimed with decomposition at near 325°C) (VIII), although it did not react with hydrogen peroxide. Both compounds, VI and VIII, showed extreme susceptibility to reduction as well as IV, and the infrared absorption spectrum similar to that of IV. On the basis of these data, it seems reasonable to assume that these two products were derived by the reaction of the same type as that which occurred in decahydroquinoline.

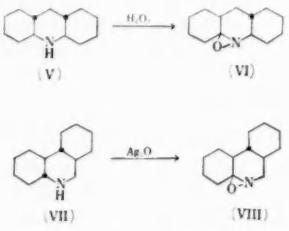


Fig. 2

In order to confirm the constitution of IV, VI and VIII, the compound IV was mainly examined since many oxidation products of decahydroquinoline have already been prepared and characterized in detail. *cis*-*N*-Benzoyldecahydroquinoline could be recovered unchanged after attempting silver oxide oxidation of it under various conditions, hence it would be expected that basic nitrogen is concerned in this reaction. On the other hand, the same product (IV) was obtained not only from *trans*(I), but also from *cis*(II) as described above. Therefore, it is considered that this reaction involves change in the nitrogen $C_{(9)}$ atoms.

As to the conversion of the bond between nitrogen and $C_{(9)}$ atom in decahydroquinoline, four possibilities are considered. The first is the formation of an *N*-hydroxyl derivative corresponding to that obtained from piperidine (IX)[9]. The second is the formation of a dimer corresponding to that produced from *N*-hydroxyl piperidine (X)[1]. The third is the formation of a nitrone and the fourth is the formation of an isonitrone***.

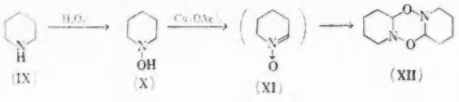


Fig. 3

(i) The new compounds, IV, VI and VIII, had no characteristic absorption of the hydroxyl group in the infrared spectra and IV did not react with phenylisocyanate as has been above mentioned. Therefore, no *N*-hydroxyl group is present in these compounds.

(ii) 1,4,2,5-Dioxa-diazine ring formed in the dimer (XII) has been reduced only by catalytic hydrogenation giving X, but not so with lithium aluminum hydride or with sulfurous acid. On the contrary, these compounds, IV, VI and VIII, were readily reduced with sodium borohydride or even with acidic potassium iodide. Hence the dimer as mentioned under the second possibility is not considered.

(iii) The new compounds, IV, VI and VIII, are similar to a nitrone in physical properties (i.e., in higher melting point or insolubility to non-polar solvents, etc.). These compounds however showed no ultraviolet absorption maxima at near 220~230 mμ[3,11,12] and no infrared absorption band at 6.25μ[12] probably due to the CN-double bond of nitrone. Therefore, it is not needful to consider the structure of nitrone for these compounds.

(iv) On the basis of these considerations three of the four possibilities described above are excluded; then the fourth is the most reasonable. It has been reported that isonitrone is readily reduced by acidic potassium iodide[11-13] and these compounds, IV, VI and VIII, also were reduced by the reagent as above mentioned. These compounds formed stable chloroplatinates although they did not form stable salts with some of the usual acids. The compound IV showed instability to any acidic reagent**** and to alkaline potassium ferricyanate[14]. As shown by these chemical behaviors, these new compounds were considered to be analogous with isonitrone. Krimm[12] reported recently that a characteristic band of isonitrone appears at near 7μ in the infrared

9) R. Wolffenstein, *Ber.*, **25**, 2777 (1892).

*** The isonitrone has a three membered ring consisting of nitrogen, oxygen and carbon atoms, and was recently named by Krimm[10]. Although the presence of this ring has been discussed for a long time, it has recently been synthesized from the Schiff base by means of hydrogen peroxide or peracetic acid. Emmons[11] suggested the name "oxazirane" for this compound.

10) H. Krimm and K. Hammann, cf. *Chem. Abstr.*, **51**, 3656 (1957).

11) W. D. Emmons, *J. Am. Chem. Soc.*, **78**, 6208 (1956).

12) H. Krimm, *Ber.*, **91**, 1057 (1958).

13) L. Horner and E. Jürgens, ibid., **90**, 2184 (1957).

**** When IV was treated with acetic anhydride it gave oily products which could not yet be characterized.

14) Oxidation of IV with alkaline potassium ferricyanate gave a neutral product, m. p. 56~57°C, which has not been characterized.

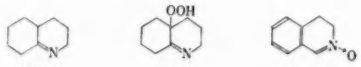
spectrum. Similar absorption was observed in these compounds, IV, VI and VIII. However, the settlement of the absorption[15] (due to near 7μ) will be deferred until more evidences are available on the various isonitrones.

In the course of the oxidation of decahydroquinoline, two pathways are considered reasonable.

i) Carbinol amine (as initial intermediate) is converted to the Schiff base by dehydration and then is further changed to isonitrone by the addition of oxygen.

ii) *N*-Hydroxyl amine (as initial intermediate) is converted to nitrone by dehydrogenation and then changed to isonitrone.

In the first case, the formation of carbinol amine has usually been observed in a reaction of tertiary amine with silver oxide[16a,b] or NBS reagent[16b]. It has been reported that the formed C(OH)–NH group is readily dehydrated to C=N-group[17]. Cohen and Witkop[6] have reported that 10-hydroperoxy-$\Delta^{1(9)}$-octahydroquinoline (XIV) is formed by the oxidation of $\Delta^{1(9)}$-octahydroquinoline (Schiff base) (XIII). Moreover, isonitrones have been obtained directly by oxidation of the Schiff base[10,11]. Accordingly, it is considered that the reaction of decahydroquinoline with silver oxide or NBS may proceed through the Schiff base stage (XIII) since the isonitrone (IV) was produced together with the hydroperoxide (XIV) in NBS oxidation as above mentioned.



(XIII) (XIV) (XV)

Fig. 4

In the second case, the formation of *N*-hydroxyl amine has commonly been observed in an oxidation of secondary amine with hydrogen peroxide[9] or perbenzoic acid[18]. It has been reported that further oxidation of *N*-hydroxylamine led to the corresponding nitrone by dehydrogenatian. If the nitrone (III) arose from the reaction of decahydroquinoline with hydrogen peroxide or perbenzoic acid, it has no stability because there is no conjugated double bond with nitrone group as shown in 3,4-dihydroisoquinoline-*N*-oxide (XV)[2]. Consequently, the nitrone (III) is converted to the corresponding isonitrone (IV). In this case, no formation of a dimer will result from a steric effect, although that point is not sure.

Further study of the other compounds related to isonitrone derived from alicyclic secondary amine series is in progress.

Experimental

Formation of Isonitrone (IV) from *trans*-Decahydroquinoline (I).—(i) *Oxidation with silver oxide.*—To a solution of 1 g. of *trans*-decahydroquinoline in 20 cc. of 30% aqueous methanol, silver oxide which was freshly prepared from 5 g. of silver nitrate was added. When the resulting suspension was warmed at 30~40°C, a silver mirror gradually formed. After 6 hr. the mixture was cooled and filtered. The methanol of the filtrate was removed under reduced pressure and the resulting aqueous solution was extracted with chloroform after being made alkaline with sodium hydroxide solution. Drying and concentration of the extract left a residue, from which 170 mg. of the product crystallized readily after the addition of ether. Unreacted *trans*-decahydroquinoline could be removed readily by means of addition of ether followed by filtration because of its great solubility in the solvent. The product insoluble in ether was recrystallized from a mixture of ethanol and ether as white needles, m.p. 280~282°C. This substance was readily soluble in polar solvents, i.e., alcohol, water or chloroform, but insoluble in non-polar solvents, i.e., ether, benzene or tetrahydrofurane. It could also be purified by sublimation at 200°C at 5 mm. and had hygroscopic property under high moisture, but did not show any change in the melting point even in that case. It could be heated over its melting points, and recovered unchanged. It formed an aurichloride, m.p. 126~127°C, and a chloroplatinate, m.p. 176~177°C.

In the infrared absorption spectrum (in Nujol) the substance showed peaks at 7.32, 7.46, 7.61, 7.80, 7.94, 8.27, 9.36, 9.53, 10.27, 10.35, 10.48, 10.81, 11.06, 11.30, 11.57, 11.86 and 12.04 μ.

Anal. Found: C, 60.72; H, 9.58; N, 7.43; H_2O_2, 13.70. Calcd. for $C_9H_{15}ON \cdot {}^3/_4\ H_2O_2$: C, 60.48; H, 9.31; N, 7.84; H_2O_2, 14.27%.

ii) *Oxidation with hydrogen peroxide.*—When a suspension of 1 g. of *trans*-decahydroquinoline in 20 cc. of 30%-hydrogen peroxide solution was left at room temperature, *trans*-decahydroquinoline dissolved during the course of the reaction and a deep orange-yellow color gradually developed. After 3 days the reaction mixture was made alkaline with concentrated ammonium hydroxide solution under cooling with water. The alkaline

15) It has been reported that the N-O-stretching vibration in amine oxide shows at near 10.6~10.8μ [R. Mathis Noel et al. *Compt rend.*, **242**, 1873 (1956)], and the characteristic absorption of grouping -O-C-N in oxazolidine ring displays at 8.63, 8.92 and 9.06μ, respectively [E. D. Bergmann, *Chem. Rev.*, **53**, 326 (1953)].

16a) H. Suginome and K. Ohno, *J. Fac. Sci. Hokkaido Univ. Ser III Chem.*, **4**, 36 (1950).

16b) O. E. Edwards, F. H. Clarke and B. Douglas, *Can. J. Chem.* **32**, 235 (1954).

17) D. H. R. Barton, *J. Chem. Soc.*, **1953**, 1027.

18) M. A. T. Rogers, ibid., **1955**, 769.

solution obtained was extracted with chloroform in as short a time as possible; the extract was washed with water and then dried with sodium sulfate. The residue that remained after evaporation of the solvent crystallized on the addition of ether. The product (185 mg.) was recrystallized from a mixture of ethanol and ether and melted at 280~282°C. It was proved to be identical (mixed melting point and comparison of infrared absorption spectra) with the product from the silver oxide oxidation.

iii) *Oxidation with perbenzoic acid.*—A solution of 100 mg. of *trans*-decahydroquinoline in 100 cc. of chloroform was treated with 150 mg. of perbenzoic acid for a day at room temperature. After this treatment, the chloroform solution afforded 13 mg. of a product which melted at 280~282°C after recrystallization and was proved to be identical also with the product obtained by the oxidation with silver oxide.

iv) *Oxidation with N-bromosuccimide (NBS).*—A solution of 1 g. of *trans*-decahydroquinoline in 40 cc. of acetone containing 10 cc. of water was treated with 1.28 g. of NBS overnight in an atmosphere of nitrogen at room temperature. The solution was then refluxed in a stream of nitrogen for 20 min. After removal of the acetone under reduced pressure the aqueous solution was extracted with ether. The ethereal extract was subjected successively to drying, removal of the solvent and distillation in vacuo. The distillate obtained at 52~53°C at 5 mmHg consisted mainly of unreacted *trans*-decahydroquinoline. The distillate obtained above the temperature of 52~53°C deposited as needle crystals on being allowed to stand in an ice box cooled at −5°C. Separation by filtration and recrystallization from ethyl acetate led to a product which melted at 96~98°C, and was positive to the starch-potassium iodide test. Its crystal form changed from needle to plate on standing. From these properties the product appeared to be identical with 10-hydroperoxy-$\Delta^{1(9)}$-octahydroquinoline, but it was necessary to carry out a further investigation for the identification because of the shortage of the material. On standing for several weeks the mother liquor of the above crystals deposited a further amount of crystals. This compound had m.p. 280~282°C after recrystallization from a mixture of ethanol and ether. It showed no depression on admixture with isonitrone (IV) obtained by the oxidation with silver oxide.

Formation of Isonitrone (IV) from *cis*-Decahyhdroquinoline (II).—When *cis*-decahydroquinoline was treated with silver oxide or hydrogen peroxide under the same conditions as *trans*-decahydroquinoline was, it produced the same isonitrone (IV) which was confirmed by the mixed melting point method and the comparison of infrared spectra.

Action of Silver Oxide on *cis*-*N*-Benzoyl-decahydroquinoline.—*cis*-*N*-Benzoyl-decahydroquinoline was nearly inert to the reagent at 30~40°C under the conditions as described under oxidation of *trans*-decahydroquinoline. Furthermore, the compound proved to be inert to silver oxide even at 80~90°C in aqueous methanol.

Reduction of Isonitrone (IV).—i) *Reduction with sodium borohydride.*—A solution of 10 mg. of sodium borohydride in 2 cc. of methanol was added to a solution of 40 mg. of isonitrone (IV) in 2 cc. of methanol under cooling with water. After having been heated for 30 min. on a steam bath, the solution was concentrated to near dryness under reduced pressure. The residue was then taken up in ether, washed with water, dried and evaporated to dryness. There were thus obtained 34 mg. of crystals which were recrystallized from petroleum ether, m.p. 46~48°C, and proved identical with *trans*-decahydroquinoline[19] by mixed melting point not only as free base but also as hydrochloride.

ii) *Reduction with sulfurous acid.*—Sulfur dioxide was saturated into a solution of 50 mg. of isonitrone (IV) in 5 cc. of water under cooling with water. After being kept for two days the resulting solution was alkalized with sodium carbonate solution and extracted with chloroform. After drying, evaporation of the extract left a residue which crystallized on standing for a few hours, giving 23 mg. of the product. On recrystallization from petroleum ether the product melted at 46~48°C and was proved identical with *trans*-decahydroquinoline.

iii) *Reduction with acidic potassium iodide.*—To a solution of 82 mg. of isonitrone (IV) in 1 cc. of 2 N-hydrochloric acid was added 1 cc. of an aqueous solution saturated with potassium iodide. On standing at room temperature iodine was gradually separated. After being kept overnight the mixture was concentrated to a syrup in a desiccator under reduced pressure and methanol was then added. Evaporation of the methanolic solution from which inorganic salt was removed by filtration left 12 mg. of a product. On washing with ether and recrystallization from a mixture of ethylacetate and chloroform, the product melted at 274~278°C and showed no depression of the melting point by admixture with *trans*-decahydroquinoline hydrochloride.

Action of Phenylisocyanate on Isonitrone (IV).—Isonitrone (IV) did not react with phenylisocyanate in dioxane on treatment for 16 hr. at room temperature.

Oxidation of α-Perhydroacridine with Hydrogen Peroxide.—A half g. of α-perhydroacridine was treated with an excess of 30% hydrogen peroxide solution at room temperature for a week. The reaction mixture gradually colored orange-yellow. The solution was made alkaline with sodium hydroxide solution under cooling with cold water and extracted with chloroform as quickly as possible. The resulting chloroform extract was washed once with water, then dried (sodium sulfate) and concentrated to dryness. On treatment with ether, the crystals could be separated into soluble and insoluble parts for the solvent. The soluble

19) Cohen and Witkop[5] and Leonard et al. (*J. Am. Chem. Soc.*, 78, 3463 (1956)) reported that derivatives of $\Delta^{1(9)}$-octahydroquinoline were reduced to the *trans*-form of decahydroquinoline in good yields by lithium aluminum hydride reduction.

part was unchanged amine. The insoluble part was recrystallized from a mixture of chloroform-ethanol as thin plates, giving 230 mg. of the product, isonitrone (VI), which sublimed with decomposition at near 320°C. This isonitrone was completely insoluble in a non-polar solvent, less soluble in water and alcohol, and more soluble in chloroform. The VI formed a chloroplatinate, m. p. 248~250°C (decomp.) In the infrared absorption spectrum (in Nujol) the substance showed peaks at 7.32, 7.46, 7.61, 7.80, 7.96, 8.17, 8.27, 8.46, 9.12, 9.56, 9.72, 10.09, 10.35, 10.50, 10.81, 11.04 and 11.91 μ.

Anal. Found: C, 67.36; H, 10.10. Calcd. for $C_{13}H_{21}ON \cdot 3/4H_2O_2$: C, 67.06; H, 9.74%.

Oxidation of α-Perhydrophenanthridine (VII) with Silver Oxide.—A mixture of 0.5 g. of α-perhydrophenanthridine and silver oxide (freshly prepared from 2 g. of silver nitrate) in 3 cc. of methanol and 30 cc. of water was refluxed at 90~100°C on a steam bath for 3 hr. A silver mirror was gradually formed. The solids were removed by filtration and washed thoroughly with hot methanol. After removal of methanol from the combined filtrate and washings, the aqueous solution was made alkaline with sodium hydroxide solution, filtered and extracted with chloroform. On evaporation of the solvent after drying, the chloroform extract afforded crystals. Since the unchanged base (VII) was readily soluble in ether, it could be separated from the reaction product by the addition of ether. The insoluble ether part was recrystallized from a mixture of ethanol and ether as needles giving 318 mg. of the product, which sublimed with decomposition at near 325°C. The property of solubility in a polar solvent was closely like that of isonitrone (IV). This product (VIII) formed a chlorofolatinate; m.p. 228~229°C (resolidified at 121°C). In the infrared absorption spectrum (in Nujol) the substance showed peaks at 7.32, 7.46, 7.61, 7.78, 7.80, 8.17, 8.27, 8.44, 9.12, 9.58, 9.72, 10.02, 10.09, 10.35, 10.52, 10.81, 11.04 and 11.91 μ.

Anal. Found: C, 66.80; H, 9.79; H_2O_2, 11.26. Calcd. for $C_{13}H_{21}ON \cdot 3/4H_2O_2$: C, 67.06; H, 9.74; H_2O_2, 10.96%.

Reductions of Isonitrone, VI and VIII, with Sodium Borohydride.—The isonitrones, VI and VIII, were respectively reduced to the original bases, V and VII with sodium borohydride in a good yield by the same treatment as described under the reduction of isonitrone (IV).

The present research was conducted under the supervision of Professor Harusada Suginome, President of Hokkaido University. The authors are also deeply indebted to Mr. Tadashi Masamune for his interest and advice and for supplying the material.

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Studies on the Sapogenins of Dioscorea tokoro Makino. II[1]. *The Structure of Tokorogenin*

By Katsura MORITA

(Received November 4, 1958)

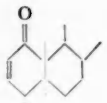
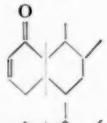
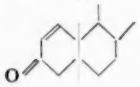
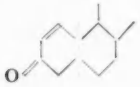
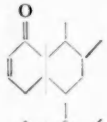
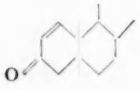
Although it was postulated that the three hydroxyl groups in tokorogenin are situated at positions 1, 2 and 3 of the steroid nucleus[2], their configuration and the nature of the A/B ring junction still remained unclarified. To make these points clear it was most desirable to establish a correlation of tokorogenin with a known sapogenin, which has been done as described in the present paper.

In the presence of a small amount of chlorosulfonic acid tokorogenin reacted with acetone and with cyclohexanone to give an isopropylidenetokorogenin (tokorogenin acetonide) and a cyclohexylidenetokorogenin, respectively. On treatment with pyridine and *p*-toluenesulfonyl chloride, the isopropylidenetokorogenin gave a tosylate, which on heating in 80% acetic acid solution furnished tokorogenin monotosylate. When the monotosylate was further treated with alkali in methanol, a crystalline, substance, soluble with difficulty, was obtained and analyzed as $C_{27}H_{42}O_4$. It was presumed to be an oxido-spirostanol,

1) This is a full paper of the previous communication (K. Morita, *Pharm. Bull.*, **5**, 494 (1957).), and constitutes Part IX of Nishikawa's paper entitled "Studies in Steroids". Part VIII: (K. Morita, This Bulletin, **32**, 476 (1959)).

2) Studies on the Sapogenins of *Dioscorea tokoro* Makino. I. (K. Morita, This Bulletin, **32**, 476 (1959).)

TABLE I

Chromophor	Substance	U. V. Spectra Max.	Log	Solvent	Ref. No
	5α-Cholest-2-en-1-one	224; 333	3.90; 1.75	C_2H_5OH	7)
	Methyl 1-keto-5β-eti-2-enate	225; 333	3.93; 1.96	C_2H_5OH	7), 8)
	Methyl 3-keto-5α-eti-1-enate	230; 323	4.07; 1.62	C_2H_5OH	7)
	Methyl 3-keto-5β-eti-1-enate	230; 323	4.12; 1.59	C_2H_5OH	9)
	25D-5β-Spirost-2-en-1-one (VII)	225; —	3.89; —	C_2H_5OH	*
	25D-5β-Spirost-1-en-3-one	232.5; —	3.99; —	C_2H_5OH	**

* This paper ** The subsequent report (Part III)

7) F. Sallman and Ch. Tamm, *Helv. Chim. Acta*, **39**, 1340 (1956).
8) W. Schlegel and Ch. Tamm, ibid., **40**, 160 (1957).
9) W. Schlegel, Ch. Tamm and T. Reichstein, ibid., **38**, 1013 (1955).

anhydrotokorogenin, from the reaction sequence. The anhydrotokorogenin gave a monoacetate and infrared absorption spectra exhibiting no characteristic band of the carbonyl group. It is, therefore, evident that the substance possesses a hydroxyl an oxido group. Oxidation of the anhydrotokorogenin with chromic anhydride-pyridine furnished a ketone, anhydrotokorogenone.

In the light of the structure of tokorogenin suggested in the previous paper[2] and the reaction sequence described above, the anhydrotokorogenone is either 2,3-oxido-spirostan-1-ol or 1,2-oxido-spirostan-3-ol. Since such an α,β-oxido-ketone has been known to undergo reduction with chromous chloride[3] giving the corresponding α,β-unsaturated ketone, the reaction was applied to the anhydrotokorogenone. As expected, anhydrotokorogenone gave an α,β-unsaturated ketone, which showed a specific U. V. absorption band at 225 mμ.

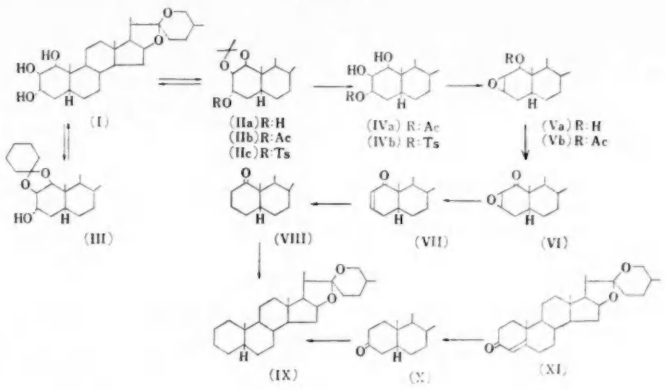
Catalytic hydrogenation of the α,β-unsaturated ketone furnished a saturated ketone, which showed marked depression of the melting point on admixture with smilagenone (X)[4]. Finally, the product from the Huang-Minlon reduction[5] of the saturated ketone proved to be identical with 25D-5β-spirostan (IX), prepared from smilagenone (X) by the known method[6]. The identity was established by the mixed melting point and the infrared absorption spectra.

The above reactions correlate tokorogenin with the known 25D-5β-spirostan (IX), and show that tokorogenin is an isosapogenin. Since the saturated ketone was not identical with smilagenone (X) as mentioned above, the structure 25D-5β-spirostan-1-one (VIII) has to be assigned to the saturated ketone from tokorogenin, and accordingly 25D-5β-spirost-2-en-1-one

3) W. Cole and P. L. Julian, *J. Org. Chem.*, **19**, 131 (1954).

4) The sample of smilagenone (X) was synthesized from diosgenin by Oppenauer oxidation followed by catalytic hydrogenation. C. Djerassi, R. Yashin and G. Rosenkranz, *J. Am. Chem. Soc.*, **74**, 422 (1952).
5) Huang-Minlon, ibid., **71**, 3301 (1949).
6) C. Djerassi and J. Fishman, ibid., **77**, 4291 (1955).

Chart 1



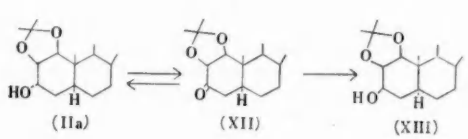
(VII) to the α,β-unsaturated ketone. These conclusions are further supported by the ultraviolet absorption spectrum of the α,β-unsaturated ketone (VII) which is in complete accord with those of known Δ^2-1-ketosteroids as shown in Table. I.

Thus, it is reasonable to assign the structure of $2\xi,3\xi$-oxido-25D-5β-spirostan-1-one to anhydrotokorogenone and that of $2\xi,3\xi$-oxido-25D-5β-spirostan-1ξ-ol to anhydrotokorogenin. Since the two hydroxyl groups in positions 1 and 2 in tokorogenin take part in the formation of the acetonide and therefore are *cis*-oriented, and the third in position 3 is *trans* to the other two, tokorogenin is either $1\alpha,2\alpha,3\beta$-triol or $1\beta,2\beta,3\alpha$-triol.

From the above arguments and on the basis of the assumption that the configuration of the hydroxyl group in position 3 of tokorogenin is α, all the reactions can be represented by the scheme shown in Chart 1.

Evidence for the α-configuration of the 3-hydroxyl group is given by the following experiment: Treatment of isopropylidenetokorogenin (IIa) with chromic anhydride-pyridine furnished isopropylidenetokorogenone (XII). Reduction of the ketone (XII) with lithium aluminum hydride gave a mixture of isopropylidenetokorogenin (IIa) and its C_3-epimer (XIII), which were separated by careful chromatography on Florisil, the latter being eluted first and then the former.

Chart 2



It has been generally accepted[8] that when a mixture of two epimeric steroidal alcohols is chromatographed, the one having an axial hydroxyl group moves more rapidly than the other. The above experiment, therefore, suggests that the 3-hydroxyl group in isopropylidenetokorogenin (IIa) is α-oriented (equatorial). In this way the structure of tokorogenin has been determined to be 25D-5β-spirostan-1β, $2\beta,3\alpha$-triol (I).

Experimental

Isopropylidenetokorogenin (Tokorogenin Acetonide) (IIa).—a) A suspension of 1 g. of tokorogenin (I) in 100 ml. of acetone containing 0.1 ml. of chlorosulfonic acid was vigorously stirred at room temperature for sixty minutes. When tokorogenin was dissolved and the acetonide was completely precipitated, the precipitates were collected, washed with ethanol and dried, m. p. 290~295°C. Yield, 1.0 g.

For analysis the substance was recrystallized from a large volume of hot methanol or dimethylformamide, m. p. 309~312°C.

Anal. Found: C, 73.50; H, 9.90. Calcd. for $C_{30}H_{48}O_5$: C, 73.73; H, 9.90%.

b) A solution of 100 mg. of tokorogenin in 100 ml. of acetone containing 50 mg. of *p*-toluenesulfonic acid was boiled under reflux for three hours and the solution was allowed to stand at room temperature overnight to separate fine needles of tokorogenin acetonide, m.p. 300~305°C, mixed m. p. with the above specimen, 305~309°C. When the acetonide was boiled in 80% acetic acid for several minutes and the solution was cooled, tokorogenin was precipitated in colorless needles melting at 273~275°C.

Cyclohexylidenetokorogenin (III).—Tokorogenin in cyclohexanone was treated with a few drops of chlorosulfonic acid under the conditions

described in the case of the acetonide. Recrystallization of the crude product from methanol furnished III melting at 288~290°C.

Anal. Found: C, 74.91; H, 10.04. Calcd. for $C_{33}H_{52}O_5$: C, 74.96; H, 9.91%.

When the cyclohexylidene compound (III) was boiled in ethanol containing a few drops of hydrochloric acid for one hour, tokorogenin was recovered.

Isopropylidenetokorogenin Acetate (IIb). — Isopropylidenetokorogenin (IIa) was acetylated by the usual means with pyridine and acetic anhydride to give the acetate (IIb), m.p. 207~208°C.

Anal. Found: C, 72.42; H, 9.70. Calcd. for $C_{32}H_{50}O_6$: C, 72.41; H, 9.50%.

Tokorogenin Monoacetate (IVa).—Isopropylidenetokorogenin acetate (IIb) was boiled in 80% acetic acid and the solution was cooled to separate colorless needles of tokorogenin monoacetate (IVa). The analytical sample recrystallized from methanol melted at 237~239°C.

Anal. Found: C, 70.75; H, 9.61. Calcd. for $C_{29}H_{46}O_6$: C, 70.98; H, 9.45%.

Isopropylidenetokorogenin Tosylate (IIc). —To a solution of 2.3 g. of isopropylidenetokorogenin (IIa) in 80 ml. of pyridine 5 g. of *p*-toluenesulfonyl chloride was added and the mixture was kept at 50°C for one hour and then at room temperature for two days. Then a large volume of water was added and the precipitate of the crude tosylate (IIc) was filtered, washed with water, and dried. Recrystallization from ether afforded colorless platelets melting at 198°C followed by immediate decomposition to a tar. Yield, 2.0 g.

Anal. Found: C, 68.94; H, 8.63. Calcd. for $C_{37}H_{54}O_7S$: C, 69.13; H, 8.47%.

Tokorogenin Monotosylate (IVb).—A suspension of 500 mg. of isopropylidenetokorogenin tosylate (IIc) in a small volume of 80% acetic acid was heated on a steam bath for twenty minutes till the solution became clear. The solution was then cooled to furnish colorless needles, m.p. 192°C (decomp.). Yield, 370 mg.

Anal. Found: C, 67.28; H, 7.96. Calcd. for $C_{34}H_{50}O_7S$: C, 67.75; H, 8.36%.

2β,3β-Oxido-25D-5β-spirostan-1β-ol (Anhydrotokorogenin) (Va).—A methanol solution of 2.0 g. of potassium hydroxide was added to a solution of 1.0 g. of tokorogenin monotosylate (IVb) in 80 ml. of methanol and the solution was boiled under reflux for one hour and cooled. The hardly soluble crystalline solid was collected, washed with methanol, and dried, m.p. 237~239°C. Yield, 500 mg.

Anal. Found: C, 75.44; H, 9.88. Calcd. for $C_{27}H_{42}O_4$: C, 75.31; H, 9.83%.

2β,3β-Oxido-25D-5β-spirostan-1β-ol Acetate (Vb). — A portion of 2β,3β-oxido-25D-5β-spirostan-1β-ol (Va) was acetylated by the usual means with pyridine and acetic anhydride to furnish the acetate (Vb) as colorless prisms melting at 246~249°C.

Anal. Found: C, 73.51; H, 9.49. Calcd. for $C_{29}H_{44}O_5$: C, 73.69; H, 9.38%.

2β,3β-Oxido-25D-5β-spirostan-1-one (Anhydrotokorogenone) (VI). — To a solution of 800 mg. of 2β,3β-oxido-25D-5β-spirostan-1β-ol (Va) in 50 ml. of pyridine was added with vigorous stirring 1.0 g. of chromic anhydride in small portions. The reaction mixture was gradually heated to 40°C and was kept at this temperature for three hours and then at room temperature for twenty-four hours. Water was added and the mixture was extracted with ether. The ethereal solution was thoroughly washed and dried, and evaporation afforded 700 mg. of needles, m.p. 238~239°C, I.R. in Nujol λ_{max} 5.86 μ (1-c=o).

Anal. Found: C, 75.35; H, 9.40. Calcd. for $C_{27}H_{40}O_4$: C, 75.66; H, 9.41%.

25D-5β-Spirost-2-en-1-one (VII).—To a suspension of 650 mg. of 2β,3β-oxido-25D-5β-spirostan-1-one (VI) in 5 ml. of acetic acid was added 20 ml. of a chromous chloride solution[10] at one time with vigorous stirring in nitrogen stream. The oxide (VI) dissolved immediately and soon 25D-5β-spirost-2-en-1-one (VII) was precipitated. Water was added and the mixture was extracted with ether. The ethereal solution was thoroughly washed and dried and evaporation furnished colorless needles, m.p. 222~223°C. Yield, 320 mg.; U.V. in EtOH λ_{max} 225 mμ (ε: 7690).

Anal. Found: C, 78.54; H, 9.51. Calcd. for $C_{27}H_{40}O_3$: C, 78.59; H, 9.77%.

25D-5β-Spirostan-1-one (VIII).—A solution of 300 mg. of 25D-5β-spirost-2-en-1-one (VII) in 50 ml. of methanol was subjected to catalytic hydrogenation over 1 g. of 5% palladium-charcoal catalyst. When 16 ml. of hydrogen was absorbed in five minutes the catalyst was removed and the filtrate was evaporated to give colorless prisms, m.p. 183~184°C. Yield, 220 mg.

Anal. Found: C, 78.17; H, 10.00. Calcd. for $C_{27}H_{42}O_3$: C, 78.21; H, 10.21%.

25D-5β-Spirostan (IX). — a) A mixture of 150 mg. of 25D-5β-spirostan-1-one (VIII), 5 ml. of diethylene glycol and 0.2 ml. of 80% hydrazine hydrate was heated to 160~170°C till the solution became clear. Potassium hydroxide (300 mg.) was added to the solution and the temperature was gradually raised to 200°C and kept there for two hours. After cooling, water was added and the mixture was extracted with petroleum ether. Evaporation of the thoroughly washed and dried extract furnished a crystalline solid. Recrystallization from methanol containing ether afforded colorless platelets, m.p. 136~137°C. Yield, 98 mg.

Anal. Found: C, 80.62; H, 11.05. Calcd. for $C_{27}H_{44}O_2$: C, 80.94; H, 11.07%.

b) Smilagenone (X) was subjected to the same treatment as the above to give 25D-5β-spirostan (IX).

Comparison of the I.R.-spectra and mixed melting point determination with the two specimens showed that they were in complete accord in all respects.

25D-5β-Spirostan-1β, 2β-diol-3-one Acetonide (Tokorogenone Acetonide) (XII).—To a solution of 1 g. of tokorogenin acetonide (IIa) in

10) A solution of chromous chloride was prepared by the method of Cole and Julian[21].

150 ml. of pyridine was added 700 mg. of chromic anhydride in small portions with vigorous agitation. Temperature was kept at 45～50°C for forty hours, and stirring was continued throughout this time. After cooling, the mixture was diluted with a large volume of water and extracted with ether. The ether solution was thoroughly washed, dried and evaporated. Recrystallization of the residue from methanol yielded colorless needles melting at 225～228°C. Yield, 800 mg. The analytical sample recrystallized from the same solvent melted at 229～231°C. I.R. in Nujol, λ_{max} 5.80 μ (3-c=o).

Anal. Found: C, 73.98; H, 9.29. Calcd. for $C_{30}H_{46}O_5$: C, 74.03; H, 9.53%.

Lithium Aluminum Hydride Reduction of 25D-5β-Spirostan-1β, 2β-diol-3-one Acetonide (Tokorogenone Acetonide) (XII).—A solution of 300 mg. of $LiAlH_4$ in 50 ml. of anhydrous ether was added in small portions to a solution of 200 mg. of 25D-5β-spirostan-1β, 2β-diol-3-one acetonide (XII) in 150 ml. of the same solvent. After being left to stand overnight at room temperature, the reaction mixture was poured into ice-water and extracted with methylene chloride. The organic layer was washed with water, dried, and evaporated to give a crystalline solid, which was re-dissolved in methylene chloride and subjected to careful chromatography on Florisil.

Fraction 1 (30 ml., CH_2Cl_2),
needles, 20 mg., m. p., 204～206°C
Fraction 2 (30 ml., CH_2Cl_2),
needles, 50 mg., m. p., 208～210°C
Fraction 3 (30 ml., CH_2Cl_2),
needles, 35 mg., m. p., 210～240°C
Fraction 4 (30 ml., CH_2Cl_2),
needles, 35 mg., m. p., 295～300°C
Fraction 5 (50 ml., CH_2Cl_2)

Fraction 6 (50 ml., ether)

The substances from Fractions 1 and 2 were the same and did not show depression of m. p. on admixture. They were combined and recrystallized to give an analytical sample, m. p. 208～210°C.

Anal. Found: C, 73.77; H, 9.67. Calcd. for $C_{30}H_{48}O_5$: C, 73.73; H, 9.90%.

As already discussed it is 25D-5β-spirostan-1β, 2β, 3β-triol 1,2-acetonide (XIII).

The substance from Fraction 4 proved to be identical with tokorogenin acetonide (IIa), and the substance from Fraction 3 is, therefore, very likely a mixture of IIa and XIII.

Summary

(1) The correlation of tokorogenin (I) with the known steroid, 25D-5β-spirostan (IX), was established: Tokorogenin formed an acetonide (IIa), which could be tosylated and then hydrolyzed to give tokorogenin monotosylate (IVb). On treatment with alkali, IVb was led to anhydrotokorogenin (Va), which on oxidation with Py.–CrO_3 and subsequent reduction with $CrCl_2$ gave rise to an α,β-unsaturated ketone (VII). Catalytic hydrogenation of VII followed by the Huang-Minlon reaction furnished 25D-5β-spirostan (IX).

(2) In order to determine the configuration of the hydroxyl group at C_3, IIa was oxidized with Py.–CrO_3 and the product was reduced with $LiAlH_4$ to give a mixture of IIa and XIII. Careful chromatography of the mixture revealed that the substance eluted first was XIII, while the second which eluted from the column was IIa, thus leaving only the structural possibility of 25D-5β-spirostan-1β, 2β, 3α-triol (I) to tokorogenin.

The author wishes to express his grateful thanks to Dr. Y. Asahina of the University of Tokyo, Dr. S. Kuwada and Dr. T. Matsukawa of Takeda Research Laboratories, for their encouragement throughout the work. Thanks are also due to Mr. H. Kamio for infrared- and ultraviolet-spectral measurements and to Mr. M. Kan for elementary analyses.

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Osaka

Studies on the Sapogenins of Dioscorea tokoro Makino. III[1]. *Synthesis of Isorhodeasapogenin and Some Reactions of Tokorogenin*

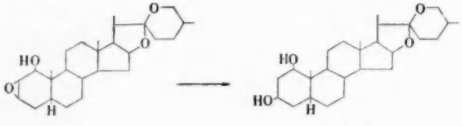
By Katsura MORITA

(Received November 4, 1958)

In order to obtain further information concerning the configuration of the hydroxyl groups in tokorogenin, the following reactions were investigated.

Reduction of anhydrotokorogenin (I) with lithium aluminum hydride in anhydrous ether caused ring-opening of the oxide giving a new dihydroxysapogenin, desoxytokorogenin. Since this dihydroxysapogenin neither formed an acetonide nor suffered oxidation by means of periodic acid and lead tetraacetate, the two hydroxyl groups in this substance have to be located at carbon atoms C_1 and C_3. As lithium aluminum hydride reduction of an oxide in the cyclohexane series is known to result in formation of an axial hydroxyl bond[2], the configuration of the hydroxyl group in position 3 of desoxytokorogenin must be β; that is, the structure of 25D-5β-spirostan-1β, 3β-diol (II) has to be assigned to this substance.

Chart 1

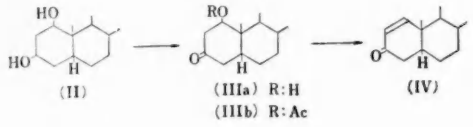


(I) (II)

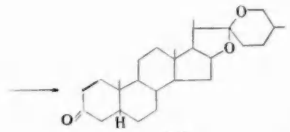
Further evidence for the structure of desoxytokorogenin (II) is given by the following reaction sequence:

Desoxytokorogenin (II) was oxidized with *N*-bromoacetamide to 25D-5β-spirostan-1β-ol-3-one (IIIa), which was acetylated and then treated with activated alumina giving 25D-5β-spirost-1-en-3-one (IV)[3]. The U.V.-absorption spectrum of this substance (IV) showed a good identity with those of known Δ^1-3-ketosteroids[4]. Upon catalytic hydrogenation over Pd/$CaCO_3$ IV yielded smilagenone (V)[5].

Chart 2



(II) (IIIa) R:H (IIIb) R:Ac (IV)



(V)

Some years ago, Nawa[6] isolated a new dihydroxysapogenin, rhodeasapogenin, from *Rhodea japonica* Roth. and suggested that it was 25L-5β-spirostan-2β, 3α-diol on the basis of various reactions, none of which led to a known steroid. Djerassi[7] attempted the oxidation of isorhodeasapogenin, an acid isomerization product of rhodeasapogenin, with chromic anhydride with the aim of obtaining a dibasic acid, isorhodeasapogenic acid, which he supposed to be identical with one of his four 2, 3- and 3, 4-seco-sapogenic acids. Unfortunately, the acid obtained by Djerassi was identical with none of his four sapogenic acids.

Quite recently, Takeda et al.[8] isolated a new dihydroxysapogenin, yonogenin, from *Dioscorea tokoro* Makino and defined its structure as 25D-5β-spirostan-2β, 3α-diol, which was the very one suggested

1) This is a full paper of the previous commuication (K. Morita, *Pharm. Bull.*, **5**, 496 (1957).), and constitutes Part X of Nishikawa's paper entitled "Studies in Steroids". Part IX: K. Morita, This Bulletin, **32**, 791 (1959).

2) M. S. Newman, "Steric Effects in Organic Chemistry", John Wiley & Sons, Inc., New York (1956), p. 130.

3) A similar reaction sequence was reported by W. Schlegel et al. (*Helv. Chim. Acta*, **38**, 1013 (1955).), who synthesized methyl 3-oxo-1-etienate from methyl 1β,3β-dihydroxyetianate.

4) See Table I in the foregoing paper (Part II) of this series.

5) The sample of smilagenone was synthesized from diosgenin by Oppenauer oxidation followed by catalytic hydrogenation.

6) H. Nawa, *J. Pharm. Soc. Japan* (*Yakugaku Zasshi*), **73**, 1192 (1953).

7) C. Djerassi and J. Fishman, *J. Am. Chem. Soc.*, **77**, 4291 (1955).

8) K. Takeda, T. Okanishi and A. Shimaoka, *J. Pharm. Soc. Japan* (*Yakugaku Zasshi*), **77**, 822 (1957).

for isorhodeasapogenin. The present author also isolated the sapogenin from the same plant and confirmed that yonogenin was not identical with isorhodeasapogenin[9].

In the course of the present investigations it was noticed that the melting points of desoxytokorogenin (II) and its diacetate were similar to those of isorhodeasapogenin and its diacetate, respectively. Similarly, the melting points of tokorogenic acid[10] and its dimethyl ester[10] were found to be in close proximity to those of isorhodeasapogenic acid and its dimethyl ester, respectively.

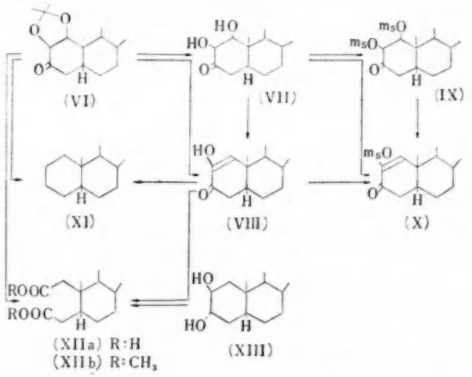
Most of the evidence for a glycol structure of rhodeasapogenin had been sought by Nawa in the fact that the sapogenin underwent ready oxidation to a dibasic acid, rhodeasapogenic acid, but it seemed probable that desoxytokorogenin (II) would be able to undergo oxidation with the same reagent to an intermediate 1,3-diketone, which would enolize and suffer further oxidation to a dibasic acid, namely, tokorogenic acid. Comparison of the I.R.-spectra and determination of the mixed melting points proved that desoxytokorogenin (II) is identical with isorhodeasapogenin, and tokorogenic acid with isorhodeasapogenic acid. Basing on these findings, Nawa has recently corrected all the structural assignments of rhodeasapogenin and its derivatives[11].

When tokorogenone acetonide (VI) was heated with acetic acid and water, tokorogenone (VII) was obtained. Tokorogenone (VII), on heating with alkali in methanol solution, lost 1 mol. of water to give a diosphenol (VIII), $C_{27}H_{40}O_4$, U. V. λ_{max} in EtOH: 269.5 mμ (ε: 6900). Direct conversion of tokorogenone acetonide (VI) into the diosphenol (VIII) could also be effected by the action of alkali at 100°C.

Stiller et al.[12] reported that selenium dioxide oxidation of cholestanone gave a mixture of cholest-1-en-2-ol-3-one (diosphenol A) and cholest-3-en-3-ol-2-one (diosphenol B). They also demonstrated that in equilibrium diosphenol A predominated in alkaline medium, while diosphenol B in acidic solution. The diosphenol (VIII) from tokorogenone (VII), however, was transformed in a mineral acid solution into an unidentified isomeric substance ($C_{27}H_{40}O_4$), from which the diosphenol (VIII) could no longer be recovered by any means. This discrepancy seems to be due to the fact that cholestanone and its diosphenols are 5α-steroids (allo-series) while tokorogenone (VII) and its diosphenol (VIII) are 5β-steroids (normal-series).

Tokorogenone (VII), on treatment with mesyl chloride and pyridine, gave a mixture of a dimesylate (IX) and an enol mesylate (X). The latter (X) was yielded also by heating the former (IX) with pyridine or with sodium iodide in acetone, and by treating the diosphenol (VIII) with mesyl chloride and pyridine. These reactions unambiguously show that the diosphenol (VIII) has to be defined as 25D-5β-spirost-1-en-2-ol-3-one.

Chart 3



It is interesting to note that the Huang-Minlon reduction of the diosphenol (VIII) as well as of tokorogenone acetonide (VI) gave 25D-5β-spirostan (XI), while the reduction of the acid isomerization product of the diosphenol (VIII) did not lead to XI.

The diosphenol (VIII) suffered oxidation with hydrogen peroxide and alkali at room temperature to give samogenic acid (XIIa)[7]. The same acid was prepared also from yonogenin by the known method, and the identity of both specimens was established by the mixed melting point determination and by the comparison of their I.R.-spectra.

Experimental

25D-5β-Spirostan-1β,3β-diol (Desoxytokorogenin) (II).—A solution of 400 mg. of 2β,3β-oxido-25D-5β-spirostan-1β-ol (anhydrotokorogenin) (I) in 50 ml. of anhydrous ether was added to a solution of 1.5 g. of lithium aluminum hydride in 60 ml. of the same solvent through a dropping

9) A sample of yonogenin was kindly given by Dr. Takeda[8] and that of isorhodeasapogenin by Dr. Nawa[6] in Takeda Research Laboratories. The mixture of these specimens melted at a temperature lower than that of either.

10) See previous paper (Part I) in this series.

11) H. Nawa, *Chem. & Pharm. Bull.*, **6**, 255 (1958).

12) E. T. Stiller and O. Rosenheim, *J. Chem. Soc.*, **1938**, 353.

funnel with stirring. The reaction mixture was stirred for two hours at room temperature and poured into a large volume of ice-water, 10% sulfuric acid was added, and the mixture was extracted with ether. The ether solution was thoroughly washed, dried, and evaporated to give colorless needles, m. p. 236~238°C. Yield, 310 mg. Recrystallization from methanol raised the m. p. to 240~242°C.

Anal. Found: C, 74.82; H, 10.46. Calcd. for $C_{27}H_{44}O_4$: C, 74.96; H, 10.25%.

On admixture with a sample of isorhodeasapogenin the melting point of the diol (II) was not depressed. The infrared spectra also established the identity of the two specimens.

Treatment of the diol (II) with acetic anhydride and pyridine at room temperature for twenty-four hours furnished the diacetate, m. p. 207~209°C.

Anal. Found: C, 72.12; H, 9.64. Calcd. for $C_{31}H_{48}O_6$: C, 72.06; H, 9.36%.

The substance thus obtained showed a good identity with isorhodeasapogenin diacetate in all respects.

25D-5β-Spirostan-1β-ol-3-one (IIIa).—25D-5β-Spirostan-1β, 3β-diol (II) (200 mg.) was added to a solution of 139 mg. of *N*-bromoacetamide in 20 ml. of 90% acetone and the mixture was warmed on a steam bath for a short time to clear the solution. After one hour, a portion of the solution was titrated with 1/10-N sodium thiosulfate solution and potassium iodide and it was indicated that the reaction proceeded stoichiometrically. A large volume of water was added and the mixture was extracted with ether. The ethereal solution was washed, dried and evaporated to dryness. Recrystallization of the residue from methanol afforded colorless needles melting at 232~233°C (decomp.).

Anal. Found: C, 74.96; H, 9.63. Calcd. for $C_{27}H_{42}O_4$: C, 75.31; H, 9.83%.

25D-5β-Spirostan-1β-ol-3-one Acetate (IIIb).—25D-5β-Spirostan-1β-ol-3-one (IIIa) (70 mg.) was acetylated with acetic anhydride and pyridine to give colorless needles of the acetate (IIIb), m. p. 200~201°C.

Anal. Found: C, 73.66; H, 9.31. Calcd. for $C_{29}H_{44}O_5$: C, 73.69; H, 9.38%.

25D-5β-Spirost-1-en-3-one (IV).—A solution of 70 mg. of IIIb was passed through unwashed alumina to furnish 50 mg. of platelets melting at 191~192°C. U. V. λ_{max} in EtOH: 232.5 mμ (ε: 9700).

Anal. Found: C, 78.55; H, 9.63. Calcd. for $C_{27}H_{40}O_3$: C, 78.59; H, 9.77%.

25D-5β-Spirostan-3-one (Smilagenone) (V).—A solution of 35 mg. of 25D-5β-spirost-1-en-3-one (IV) in 30 ml. of methanol was subjected to catalytic hydrogenation over 5% palladium-charcoal catalyst in an atmospheric pressure. The solution rapidly took up 1.6 ml. of hydrogen and the reaction almost stopped. The catalyst was removed and the filtrate was concentrated under diminished pressure to give colorless platelets. Recrystallization from methanol afforded the pure material melting at 183~184°C.

The sample here obtained showed no depression of the melting point on admixture with an authentic specimen prepared from diosgenone by the known method[5].

25D-5β-Spirostan-1β, 2β-diol-3-one (Tokorogenone) (VII).—25D-5β-Spirostan-1β, 2β-diol-3-one acetonide (VI) (100 mg.) in 3 ml. of 80% acetic acid was heated on a steam bath for forty minutes. The resulting solution was evaporated under diminished pressure to give a crystalline solid (VII), which upon recrystallization from methanol afforded thin plates melting at 224~227°C. Yield, 60 mg.

Anal. Found: C, 72.54; H, 9.57. Calcd. for $C_{27}H_{42}O_5$: C, 72.65; H, 9.42%.

A small portion of the diol (VII) was acetylated with acetic anhydride and pyridine by the usual means. Recrystallization of the crude acetate from methanol furnished colorless needles, m. p. 223~226°C.

Anal. Found: C, 70.10; H, 8.59. Calcd. for $C_{31}H_{46}O_7$: C, 70.16; H, 8.74%.

25D-5β-Spirostan-1β,2β-diol-3-one Dimesylate (IX) and 25D-5β-Spirost-1-en-2-ol-3-one Mesylate (X).—a) Mesyl chloride (1 ml.) was added to a solution of 500 mg. of 25D-5β-spirostan-1β, 2β-diol-3-one (VII) in 10 ml. of pyridine at 0°C and the solution was allowed to stand at room temperature in a dark place for three days. A large volume of water was added and the mixture was extracted with ether. The ether solution was thoroughly washed with water, dried and evaporated to furnish almost colorless needles of the dimesylate (IX), m. p. 223°C (decomp.). Yield, 340 mg.

Anal. Found: C, 57.71; H, 7.66. Calcd. for $C_{29}H_{46}O_9S_2$: C, 57.78; H, 7.69%.

The mother liquor from the above dimesylate (IX) was further concentrated and left overnight to give different crystals, m. p. 222~223°C. Yield, 120 mg. The substance here obtained showed a marked depression of the melting point on admixture with the dimesylate (IX). On the basis of the ultraviolet absorption spectrum and elementary analyses structure X was assigned to this substance. U. V. λ_{max} in EtOH: 238.5 mμ (ε: 7100).

Anal. Found: C, 66.10; H, 8.20. Calcd. for $C_{29}H_{42}O_6S$: C, 66.38; H, 8.36%.

b) A solution of 200 mg. of 25D-5β-spirostan-1β, 2β-diol-3-one dimesylate (IX) in 8 ml. of acetone containing 500 mg. of sodium iodide was heated in a sealed tube at 120°C for twenty-four hours. After cooling, the reaction mixture was diluted with water and extracted with ether. The ethereal solution was washed with water and then with sodium thiosulfate solution, dried, and evaporated to furnish colorless crystals, m. p. 222~223°C.

c) A portion of 25D-5β-spirost-1-en-2-ol-3-one (VIII) dissolved in pyridine was treated with mesyl chloride by the usual means. Dilution of the reaction mixture with water followed by washing, drying and evaporation afforded the same mesylate, m. p. 222~223°C.

25D-5β-Spirost-1-en-2-ol-3-one (Diosphenol) (VIII).—a) A solution of 25D-5β-spirostan-1β,2β-

diol-3-one (VII) (70 mg.) in 5 ml. of methanol containing 500 mg. of potassium hydroxide was boiled on a steam bath for thirty minutes. After cooling and diluting with a large volume of water, the mixture was extracted with methylene chloride. The organic layer was then washed, dried, and evaporated to give colorless needles. Recrystallization from methanol afforded the analytical sample, m. p. 227~228°C. Yield, 40 mg. U. V. λ_{max} in EtOH: 269.5 mμ (ε: 6900).

Anal. Found: C, 75.49; H, 9.37. Calcd. for $C_{27}H_{40}O_4$: C, 75.66; H, 9.41%.

b) A portion of 25D-5β-spirostan-1β, 2β-diol-3-one acetonide (VI) was treated with potassium hydroxide as described and the resulting solution was worked up as above to give the same diosphenol (VIII); mixed melting point with the specimen from a, 227~228°C.

Acid Isomerization of 25D-5β-Spirostan-1β, 2β-diol-3-one (VII), 25D-5β-Spirostan-1β, 2β-diol-3-one Acetonide (VI) and 25D-5β-Spirost-1-en-2-ol-3-one (VIII).—a) A solution of 70 mg. of 25D-5β-spirostan-1β, 2β-diol-3-one (VII) in 5 ml. of methanol containing 0.2 ml. of concentrated hydrochloric acid was boiled under reflux for thirty minutes. After concentration under reduced pressure, water was added and the mixture was extracted with methylene chloride. Thorough washing with water followed by drying and evaporation furnished a crystalline solid, m. p. 245~248°C. Recrystallization from methanol raised the m. p. to 254~255°C. The ultraviolet absorption spectrum of this substance showed a slight shift to a lower wavelength than that of the alkali isomerization product VIII, i. e., U. V. λ_{max} in EtOH: 267 mμ (ε: 5700), no hydroxyl absorption bands being noticed.

Anal. Found: C, 75.49; H, 9.37. Calcd. for $C_{27}H_{40}O_4$: C, 75.66; H, 9.41%.

b) 25D-5β-Spirostan-1β, 2β-diol-3-one acetonide (VI) was subjected to acid isomerization under the conditions described above. The crude product after recrystallization from methanol showed the same melting point as that of the specimen from a.

c) A solution of 70 mg. of 25D-5β-spirost-1-en-2-ol-3-one (VIII) in 5 ml. of methanol containing 0.2 ml. of concentrated hydrochloric acid was boiled under reflux for thirty minutes. Working up of the reaction mixture by the same procedure as described in a and b yielded fine needles melting at 254~255°C.

All the specimens from a, b and c were confirmed to be identical with one another by mixed melting point determination.

25D-5β-Spirostan (XI).—25D-5β-Spirostan-1β, 2β-diol-3-one acetonide (VI) (500 mg.) was dissolved in 20 ml. of diethylene glycol containing 1 ml. of 80% hydrazine hydrate and 2.0 g. of potassium hydroxide. The mixture was heated at 200°C in an oil bath for three hours. After cooling, the reaction mixture was diluted with a large volume of water and extracted with ether. The ethereal solution was washed with water, dried, concentrated, and chromatographed on Florisil. 25D-5β-Spirostan (XI) was eluted from the column by petroleum ether and recrystallization from methanol-petroleum ether gave the analytical sample melting at 136~137°C. Identity of the substance here obtained was confirmed by comparison of the I. R.-spectra and the mixed melting point determination with an authentic specimen. When 25D-5β-spirostan-1β, 2β-diol-3-one (VII) and 25D-5β-spirost-1-en-2-ol-3-one (VIII) were subjected to the same reaction, 25D-5β-spirostan (XI) was obtained.

Samogenic Acid (XIIa).—Thirty per cent hydrogen peroxide (1 ml.) was added to a solution of 300 mg. of 25D-5β-spirost-1-en-2-ol-3-one (diosphenol) (VIII) in 5 ml. of methanol containing 200 mg. of potassium hydroxide and the solution was left standing at room temperature for one hour. A large volume of water was added, the resulting clear solution was extracted once with ether, and the ether solution was discarded. The aqueous solution was acidified and extracted with ether and the ethereal solution was washed with water, dried and evaporated to give a crystalline solid. Recrystallization of the solid from methanol furnished colorless thin plates melting at 271~273°C. Yield, 200 mg.

By the action of diazomethane, the acid (XIIa) afforded the dimethyl ester (XIIb), m. p. 147~148°C, $[\alpha]_D^{31}$: −28° (*c*; 0.5% in $CHCl_3$).

Summary

(1) Reduction of anhydrotokorogenin with lithium aluminum hydride led to a new dihydroxysapogenin, desoxytokorogenin; the structure 25D-5β-spirostan-1β, 3β-diol was assigned on the basis of various reactions and theoretical considerations.

(2) Desoxytokorogenin, 25D-5β-spirostan-1β, 3β-diol, was incidentally found to be identical with isorhodeasapogenin, the structure of which had so far been left unclarified.

(3) Identity of tokorogenic acid with isorhodeasapogenic acid was also confirmed.

(4) Tokorogenin was correlated with samogenic acid and yonogenin via a diosphenol, 25D-5β-spirost-1-en-2-ol-3-one, whose structure was unambiguously established.

The author wishes to express his grateful thanks to Dr. Y. Asahina of the University of Tokyo, Dr. S. Kuwada and Dr. T. Matsukawa of Takeda Research Laboratories for their encouragement throughout the work. Thanks are also due to Dr. K. Takeda of Shionogi Research Laboratories for the gift of a sample of yonogenin, to Mr. H. Kamio for infrared- and ultraviolet-spectral measurements and to Mr. M. Kan for elementary analyses.

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Studies on the Sapogenins of Dioscorea tokoro Makino. IV[1]. *The Contents of Tokorogenin, Yonogenin and Diosgenin*

By Katsura MORITA

(Received November 4, 1958)

Until recently, three steroids of natural origin possessing a hydroxyl group in position 1 had been announced. They are ouabagenin[2], acovenosigenin A[3], both being cardiac aglycones, and ruscogenin[4], a steroidal sapogenin isolated quite recently by C. Sannié et al. from *Ruscus aculeatus* L. and defined by Benn et al.[5] as 25D-spirost-5-en-1ξ, 3β-diol. Tokorogenin and rhodeasapogenin[6] are further additions to the examples of 1-hydroxylated steroids of natural origin. Tokorogenin is the only known steroid possessing a glycerol moiety in ring A, its structure having been defined by the author as 25D-5β-spirostan-1β, 2β, 3α-triol.

As described in a previous paper[7], tokorogenin was isolated from the rhizomes of *D. tokoro* Makino in a poor yield compared with diosgenin, which had been regarded as the sole steroidal sapogenin in the same plant. In the course of the present investigation, however, it was noticed that the rhizomes of *D. tokoro* Makino collected at Gotenba in Shizuoka Prefecture yielded extraordinarily large amounts of tokorogenin and a new sapogenin[8] and a minute quantity of diosgenin, compared with those collected in other places. No difference in appearance could be found between the rhizomes and the plants collected at Gotenba and those from other places.

In the light of these findings it was presumed that the rhizomes of *D. tokoro* Makino from certain districts other than Gotenba might be an excellent source of tokorogenin or other sapogenins, and the author started investigations on the sapogenin contents in the same plant species from various districts in Japan.

For this purpose, dried and sliced rhizomes collected at various sites were subjected to digestion with 1.2-N hydrochloric acid for six hours followed by drying and extraction with ether in a Soxhlet apparatus. The ether extract separated a voluminous jelly comprising tokorogenin, yonogenin and other unknown impurities. The jelly yielded rather impure tokorogenin and yonogenin by chromatographic purification on Florisil, while the mother liquor yielded almost pure diosgenin.

Since the above procedure was rather troublesome and unsuitable for rapid estimation with many samples, the following process was used: The ether extract was evaporated to dryness, and the residue was dissolved in methylene chloride and chromatographed on Florisil to give a diosgenin fraction and a yonogenin-tokorogenin fraction; both fractions were then evaporated and weighed to find roughly the amount of diosgenin and the total amount of other sapogenins. The results are summarized in Table I, which shows that the amount of diosgenin and that of other sapogenins vary markedly according to the site of collection of the rhizomes. It is especially noteworthy that the rhizomes collected even in neighboring villages (No. 21—No. 25) in Gotenba showed considerable differences in their sapogenin contents.

In order to obtain further information on these points, similar experiments were carried out with the rhizomes cultivated in the Experimental Farm of our company[9], each sample being prepared from one plant and by the same process.

A methanol extract of a rhizome was

1) This communication is Part XI of Nishikawa's paper entitled "Studies in Steroids". Part X; K. Morita, This Bulletin, **32**, 796 (1959).

2) C. Mannich and C. Siewert, *Ber.*, **75**, 737 (1942); Ch. Tamm, G. Volpp and C. Baumgartner, *Helv. Chim. Acta*, **40**, 1469 (1957).

3) W. Schlegel, Ch. Tamm and T. Reichstein, ibid., **38**, 1013 (1955).

4) C. Sannié and H. Lapin, *Bull. soc. chim. France*, **1955**, 1556.

5) W. R. Benn, F. Colton and R. Pappo, *J. Am. Chem. Soc.*, **79**, 3920 (1957).

6) The previous papar (Part III) of this series; H. Nawa, *Chem. & Pharm. Bull.*, **6**, 255 (1958).

7) M. Nishikawa, K. Morita, H. Hagiwara and M. Inoue, *J. Pharm. Soc. Japan* (*Yakugaku Zasshi*), **74**, 1165 (1954).

8) This sapogenin was thereafter shown to be identical with yonogenin: K. Takeda, T. Okanishi and A. Shimaoka, ibid., **77**, 822 (1957).

9) Cultivation of the plants in the Experimental Farm was started from the rhizomes collected in the neighborhood of Gotenba and other places, and has been continued for more than three years.

TABLE I

Expt. No.	Collection site	♀ ♂	Diosgenin (%)	Yonogenin & tokorogenin (%)
1	Kongosan (Osaka)	—	1.4	0.5
2	Tachikawa (Chiba)	—	3.2	0.7
3	Mishima (Shizuoka)	—	2.5	1.0
4	Yamakita (Shizuoka)	—	1.0	1.0
5	Nagano (Nagano)	—	2.8	0.8
6	Jubuin (Kyushu)	—	2.0	0.6
7	Miyanohara (Kyushu)	—	2.7	0.8
8	Mutobe (Kyoto)	—	2.7	0.7
9	Sado (Niigata)	—	1.9	0.5
10	Suginosawa (Niigata)	—	4.1	1.6
11	Katsuyama (Fukui)	♀	2.4	1.6
12	Katsuyama (Fukui)	♂	2.0	0.6
13	Hakusanshita (Ishikawa)	♀	2.0	0.7
14	Hakusanshita (Ishikawa)	♂	2.2	0.6
15	Takarazuka (Hyogo)	♀	1.2	0.6
16	Takarazuka (Hyogo)	♂	1.3	1.7
17	Shinjuku (Tokyo)	♀	3.8	1.4
18	Shinjuku (Tokyo)	♂	3.0	1.4
19	Gotenba (Shizuoka)	♀	0.4	1.8
20	Gotenba (Shizuoka)	♂	0.6	2.8
21	Gotenba-Nagahara (Shizuoka)	—	1.4	2.3
22	Gotenba-Taniga (Shizuoka)	—	1.1	1.4
23	Gotenba-Oyama (Shizuoka)	—	0.2	2.6
24	Gotenba-Ueno (Shizuoka)	—	0.3	2.9
25	Gotenba-Subashiri (Shizuoka)	—	2.5	1.9

TABLE II

Expt. No.	Diosgenin (%)	Yonogenin (%)	Tokorogenin (%)	Expt. No.	Diosgenin (%)	Yonogenin (%)	Tokorogenin (%)
1	<0.1	0.7	0.8	26	1.1	0.2	0.3
2	<0.1	0.5	0.7	27	0.9	0.1	0.2
3	<0.1	0.6	0.8	28	0.1	0.5	0.6
4	<0.1	0.5	0.6	29	<0.1	0.7	0.8
5	<0.1	1.4	0.8	30	<0.1	0.4	0.6
6	<0.1	0.7	0.8	31	1.5	0.2	0.2
7	0.8	0.2	0.3	32	0.1	0.5	0.5
8	0.1	0.3	0.7	33	0.1	0.5	0.6
9	1.1	0.1	0.2	34	<0.1	0.6	0.7
10	0.7	0.2	0.1	35	<0.1	0.2	0.4
11	<0.1	0.9	0.6	36	<0.1	0.3	0.4
12	0.1	0.7	0.6	37	<0.1	0.5	0.7
13	0.1	0.7	0.7	38	<0.1	0.8	0.9
14	0.1	0.6	0.6	39	2.1	0.2	0.3
15	0.1	1.3	0.8	40	2.3	0.2	0.3
16	0.2	1.0	1.0	41	0.1	0.3	0.6
17	1.3	0.2	0.2	42	<0.1	1.0	0.7
18	0.2	0.6	0.7	43	1.9	0.2	0.3
19	1.1	0.1	0.3	44	1.3	0.2	0.3
20	1.7	0.2	0.3	45	2.1	0.2	0.3
21	1.0	0.2	0.3	46	<0.1	0.7	0.8
22	1.1	0.1	0.2	47	0.1	0.7	0.7
23	1.3	0.2	0.2	48	0.2	0.8	0.7
24	0.2	1.0	0.6	49	0.2	0.7	0.8
25	0.3	0.7	0.7	50	0.1	0.5	0.7

TABLE II (Continued)

Expt. No.	Diosgenin (%)	Yonogenin (%)	Tokorogenin (%)	Expt. No.	Diosgenin (%)	Yonogenin (%)	Tokorogenin (%)
51	<0.1	0.8	1.0	106	1.8	<0.1	<0.1
52	<0.1	0.2	1.1	107	0.8	<0.1	<0.1
53	0.1	1.0	1.0	108	1.2	<0.1	<0.1
54	<0.1	1.1	1.0	109	1.0	<0.1	<0.1
55	0.1	0.7	1.0	110	0.9	<0.1	<0.1
56	1.3	0.2	1.3	111	1.0	<0.1	<0.1
57	<0.1	0.5	1.8	112	0.6	<0.1	<0.1
58	<0.1	0.8	1.1	113	1.0	<0.1	<0.1
59	0.1	0.5	1.9	114	1.5	0.1	0.2
60	0.2	0.7	0.7	115	1.8	<0.1	0.2
61	1.2	0.2	0.3	116	0.2	1.0	0.6
62	0.1	0.5	0.8	117	2.3	0.2	0.3
63	0.2	0.9	0.8	118	0.2	0.5	0.6
64	0.2	0.7	0.8	119	0.2	0.6	0.7
65	0.1	0.8	0.8	120	2.0	0.1	0.2
66	0.2	0.7	0.8	121	0.3	0.7	0.6
67	0.1	0.7	0.8	122	2.3	0.3	0.2
68	0.2	0.6	0.6	123	1.7	0.1	0.2
69	0.1	0.6	0.6	124	2.1	0.2	0.3
70	0.1	0.8	0.6	125	1.2	0.1	0.2
71	<0.1	0.8	0.9	126	1.1	0.1	0.1
72	<0.1	0.7	1.1	127	2.1	0.2	0.2
73	<0.1	0.8	0.9	128	1.4	0.1	0.2
74	0.1	0.9	0.9	129	0.3	0.4	1.1
75	<0.1	0.6	1.0	130	0.2	0.4	1.0
76	0.1	0.6	0.9	131	0.3	0.8	0.8
77	0.2	0.8	1.5	132	0.1	0.4	1.2
78	<0.1	0.7	0.8	133	0.3	1.1	1.4
79	<0.1	1.1	1.0	134	0.3	0.9	1.7
80	0.3	0.5	0.8	135	0.2	0.8	1.6
81	0.3	1.0	1.2	136	0.2	0.9	1.3
82	0.2	1.6	1.1	137	0.2	1.2	1.4
83	0.1	0.3	1.1	138	0.2	0.8	1.0
84	0.2	1.3	1.1	139	1.6	0.1	0.2
85	2.2	0.2	0.4	140	0.2	0.6	0.7
86	<0.1	0.6	1.1	141	1.4	0.1	0.2
87	<0.1	1.2	1.1	142	0.2	0.9	0.7
88	0.4	0.1	<0.1	143	1.6	0.2	0.2
89	0.6	<0.1	<0.1	144	1.8	0.1	0.2
90	0.9	<0.1	<0.1	145	0.2	0.6	0.7
91	0.6	<0.1	<0.1	146	0.2	0.5	0.8
92	0.9	<0.1	<0.1	147	1.7	0.1	0.3
93	0.8	0.3	<0.1	148	0.2	0.7	1.0
94	0.7	<0.1	<0.1	149	1.3	0.1	0.2
95	1.1	<0.1	<0.1	150	1.4	0.1	0.3
96	1.1	0.1	<0.1	151	1.2	0.1	0.2
97	0.7	0.1	<0.1	152	0.3	1.0	0.9
98	0.8	0.1	<0.1	153	0.1	0.6	0.6
99	0.9	<0.1	<0.1	154	1.7	0.2	0.2
100	0.8	<0.1	<0.1	155	1.1	0.9	0.8
101	0.8	<0.1	<0.1	156	0.3	1.0	0.9
102	0.7	<0.1	<0.1	157	0.2	0.7	0.9
103	0.9	<0.1	<0.1	158	1.2	0.2	0.2
104	1.0	<0.1	<0.1	159	0.3	0.8	0.9
105	1.3	<0.1	<0.1	160	1.0	0.3	0.7

hydrolyzed with ethanolic hydrochloric acid[10], extracted with methylene chloride, chromatographed on Florisil and finally subjected to the colorimetric estimation of the three sapogenins by means of Yamagishi's method[11]. The results of the analyses tabulated in Table II reveal that the plants containing diosgenin as the major ingredient contain very small amounts of tokorogenin and yonogenin or lack them, while those containing large amounts of tokorogenin and yonogenin give only minute yields of disogenin or lack it. These findings are very interesting in view of the fact that the structures of tokorogenin and yonogenin are closely related (5β, 2β-OH, 3α-OH), while diosgenin is considerably different from these two sapogenins (Δ^5, 3β-OH). In this connection it is also interesting to point out that the Shionogi's workers have isolated the fourth sapogenin, kogagenin, from the vines and leaves of the same plant[8] and suggested a structure of 25D-spirostan-1β, 2β, 3α, 5β-tetrol for the new sapogenin[12].

Experimental

Improved Isolation of Diosgenin, Yonogenine and Tokorogenin from the Rhizomes of *D. tokoro* Makino (Collected at Gotenba). —Dried rhizomes (1 kg.) collected at Gotenba was gently heated with 4.6 l. of 1,2-N hydrochloric acid for six hours and the hydrolyate was centrifuged, and the solid was washed with water and dried to give 186 g. of a dark brown cake. The cake was then extracted with petroleum benzine in a large Soxhlet apparatus for five hours, whereby diosgenin separated out as a white crystalline solid during the extraction. Ether was then substituted for petroleum benzine and extraction was continued for twenty more hours to give voluminous precipitation of dark brown jelly, which was filtered, washed with ether and dried. It weighed 18.7 g.

TABLE III

Sample	Content		
	Diosgenin (%)	Yonogenin (%)	Tokorogenin (%)
Dried rhizomes 1 kg.	0.82	0.63	0.50
Acid hydrolysate 186 g.	4.32	3.1	2.6
Jelly 18.7 g.	—	30	24

10) Hydrolysis was carried out by Marker's standard method.
11) M. Yamagishi and I. Nakamura, *Chem. & Pharm. Bull.*, **6**, 421 (1958).
12) At the Meeting of Organic Chemistry of Naturally Occurring Substances, October 18, 1958.

The analytical data shown in Table III[13] indicate that the procedure described above is satisfactory for the separation of diosgenin and a mixture of tokorogenin and yonogenin from the rhizomes.

For the separation of tokorogenin from yonogenin, the jelly (18.7 g.) was acetylated with pyridine-acetic anhydride and the acetylated mixture dissolved in ether was repeatedly washed with dilute aqueous alkali until washings became colorless. After the ether solution was dried and evaporated, the residue was redissolved in hot ethanol and treated with charcoal. Upon the solution was cooled tokorogenin triacetate was precipitated as almost colorless leaflets melting at 250~255°C. For analysis the crude material (m. p. 250~255°C) was dissolved in methylene chloride and the solution was passed through a column of Florisil, and concentration of the solution and recrystallization of the residue from ethanol raised the m. p. to 260~263°C. Yield, 4.7 g. The mother liquor, after hydrolysis with methanol and alkali, was poured into water and extracted with ether. The ether solution was washed with water, dried and evaporated to dryness. Chromatography of a portion of the residue on Florisil furnished yonogenin from methylene chloride-ethyl acetate (4 : 1) eluates and a small amount of tokorogenin from ethyl acetate eluates. After recrystallization from hot ethanol[14] the sample of yonogenin melted at 238~240°C and was identified with an authentic sample.

Yonogenin Acetate. — A small portion of yonogenin was acetylated with pyridine and acetic anhydried to give colorless needles of the diacetate, m. p. 213°C, $[\alpha]_D^{17}$ −17° (c=1.0%, $CHCl_3$). The sample showed no depression of m. p. on admixture with an authentic specimen.

Hydrolysis of the diacetate with alkali and methanol led to needles of the free sapogenin melting at 238~240°C.

Summary

(1) Improved isolation of tokorogenin, yonogenin and diosgenin from the rhizomes of *D. tokoro* Makino collected at Gotenba is described.

(2) The sapogenin contents in rhizomes of *D. tokoro* Makino collected in various districts in Japan were examined by means of chromatography.

(3) The sapogenin contents in rhizomes of cultivated plants of *D. tokoro* Makino were examined and it was found that the plants containing diosgenin as the major ingredient contain very small amounts of tokorogenin and yonogenin or lack them, while those containing large amounts of tokorogenin and yonogenin give only minute yields of diosgenin or lack it.

13) Analyses were carried out by Yamagishi's colorimetric method[7].
14) A solution of yonogenin in organic solvents showed strong tendency to form a gel.

The author wishes to express his grateful thanks to Dr. Y. Asahina of the University of Tokyo, Dr. S. Kuwada and Dr. T. Matsukawa of Takeda Research Laboratories for their encouragement throughout the work. Thanks are also due to Dr. K. Takeda of Shionogi Research Laboratories for the gift of a sample of yonogenin, to Dr. S. Yamagishi and Mr. I. Nakamura for the analyses of the sapogenins, to Dr. T. Watanabe for the collection of the plants, and to Mr. R. Hatta of their Experimental Form in Kyoto for the growing of the plants.

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On the Crystal Growth of Zinc Sulfide Phosphor

By Yoshiro ŌTOMO

(Received November 12, 1958)

When zinc sulfide is fired, usually the flux is to be used, which 1) protects the phosphor from oxidation[1], 2) acts as the co-activator[2-4] and 3) promotes its crystallization. Concerning those functions, there have been few detailed reports on 3), the crystallization of the phosphor.

The author has made observations with an electron microscope on the process of crystallization of the phosphor, with and without flux — here, 2 wt. % of sodium chloride has been added — and, at the same time, he has determined the sizes and the forms of crystals, using a NORELCO X-ray diffractometer. It is found that, before firing, the raw material of zinc sulfide is a large aggregate of crystallites of β-form with 8% of α-form of the same material, and through firing, the process of crystal growth is much affected by the addition of flux. Also, he has discussed the effect of flux on the size of the grown crystals, the forms of crystals and their transition velocities.

Experimental Results and Discussion

The Crystal Growth and the Electron Microscope Observation.—A special replica method was used for the electron microscope observation. The phosphor powder was scattered on rock salt and Pt-Pd metal was evaporated on it obliquely from one direction. Carbon was then evaporated to cover the Pt-Pd metal and the phosphor crystal. After those procedures, rock salt was dissolved in water and zinc sulfide was dissolved in 6 N-hydrochloric acid. Thus, the Pt-Pd metal covered with carbon film was left, and was put on the mesh as a sample.

The base material of zinc sulfide phosphor was precipitated through the reaction of hydrogen sulfide gas with the solution of zinc sulfate. The precipitate was washed with de-ionized water and dried at room temperature. The precipitate was observed by the electron microscope and was found to be a large aggregate of needle-like crystallites, as is demonstrated in Fig. 1. In order to see the crystal structure of the aggregate, a NORELCO X-ray diffractometer was used and $10\bar{1}0$, 0002 and $10\bar{1}1$ patterns, the strongest patterns of α-form crystal, and 111 pattern, the strongest pattern of β-form, were checked. It was found that the raw material of zinc sulfide was not amorphous but consisted of nearly perfect crystals of β-form containing approximately 8% of α-form.

Assuming that they are perfect β-form crystals, the mean diameter of the crystals, d, is obtained from the half-peak breadth, B, of the 111 diffraction pattern, using

$$B = K\lambda/d\cos\theta \qquad (1)$$

where λ is the wavelength of X-ray and θ is the angle of diffraction. For $K \approx 1$, the diameter of the unfired zinc sulfide crystal, d, is evaluated to be about 150 Å from our X-ray diffraction measurements.

1) K. Takagi, *J. Chem. Soc. Japan, Ind. Chem. Sec. (Kogyo Kagaku Zasshi)*, **61**, 959 (1958).
2) F. A. Kröger and J. Dikhoff, *Physica* XVI, 297 (1950).
3) F. A. Krgöer, ibid., XXII, 637 (1956).
4) F. E. Williams, *J. Opt. Soc. Am.*, **47**, 869 (1957).

Fig. 1. Unfired ZnS: Ag.
Electron micrograph×5,000

In Figs. 2a and 2b, the processes of crystal growth during the firing of the precipitated zinc sulfide are shown. The processes of crystalization of the samples added with or without the flux of 2 wt. % of sodium chloride were investigated with an electron microscope. In both cases, no difference is observed up to 400°C and a slight change in the crystalline state is observed at 500°C in case of a sample with 2 wt. % of sodium chloride. At 600°C, the crystallites of zinc sulfide have grown together considerably in both cases, and, at 700°C, perfectly grown crystallites were observed with 2 wt. % of sodium chloride. But without flux, the rapid crystal growth is seen at temperatures between 800 and 900°C. However, the difference between the two cases is not only in the speed of crystal growth, but also in some other aspects of growing processes. Considerations on the later aspects are given below.

For the modes of crystal growth of such sulfides, two processes are mainly considered; the one, through the screw dislocation and the other, the surface nucleation[5].

The zinc sulfide molecule, which is adsorbed on the step of the crystal, diffuses towards the kink and forms a part of the crystal lattice, pushing the step out and making the crystal larger. The diffusion length, l_d, of zinc sulfide is given by

$$l_d=\sqrt{D\tau}$$

where D is the diffusion constant and τ is the lifetime of the molecule adsorbed on the surface.

By the addition of 2 wt. % of sodium chloride the diffusion is made more active, and D becomes larger. And, through the interaction with the flux, there will be more possibilities of forming kinks at the surface of crystals, and the mean distance, l_k, between kinks will become smaller. Hence, the relationship

$$l_d \gg l_k$$

will be satisfied easily and the growth of the steps at crystal surfaces will become independent of the crystal symmetry, resulting in the circular step-wise crystals. Such cases are given in Fig. 2a; one for the sample fired at 700°C and another for that fired at 1000°C. Without flux, the diffusion of zinc sulfide molecules along the crystal surfaces is not active, and D becomes smaller. Also, the kinks at the surfaces are not formed so easily, and l_k becomes larger.

Hence, the relationship, $l_d \gg l_k$, is no longer satisfied, resulting in the considerable influence of crystal symmetries on the growth of steps at the surfaces and the anisotropic crystal growth. Some examples are given in Fig. 2b. For the firing at temperatures above 900°C, the straight step, perpendicular to the direction of crystal growth, is seen clearly. At 1100°C, the α-form crystal of zinc sulfide is observed, especially along (0001) crystal surface, which is developed as pyramids.

Relationship between the Firing Condition and the Diameter of Crystals.—The half-peak breadth of the X-ray diffraction pattern was corrected for the characteristic width of the instrument, and the crystal sizes of various zinc sulfide phosphors were obtained by using Eq. 1.

The results are given in Fig. 3. In this diagram, the solid line shows the diameter of crystals without flux and the dotted line shows that with 2 wt. % of sodium chloride as flux. For both cases, up to 400°C, little crystal growth is observed and no difference can be seen compared with the material before firing. At about 500°C, the crystal growth begins and, at 600°C, it becomes extremely rapid. When the flux is added, the growth, at temperatures around 600°C, is especially remarkable. Those results show a rather good correspondence with the behaviors of crystal growth shown in Fig. 2.

Comparison between the measured crystal diameters obtained through the X-ray diffraction method and the electron microscope is made below.

In Fig. 2b, the picture of the sample fired, without flux, at 800°C shows that the diameter of the crystal agrees with that obtained by X-ray diffraction which

5) D. C. Reynolds and L. C. Greene, *J. Appl. Phys.*, **29**, 559 (1958).

400°C×3*h*

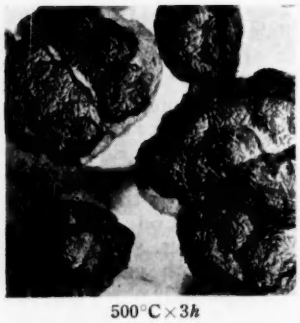
500°C×3*h*

600°C×3*h*

700°C×3*h*

1000°C×3*h*

Fig. 2a. ZnS: Ag phosphor (with added 2 wt. % NaCl as flux).
Electron micrograph×5,000


500°C×3*h*

600°C×3*h*

800°C×3*h*

900°C×3*h*

1100°C×3*h*

Fig. 2b. ZnS: Ag phosphor (without flux).
Electron micrograph×5,000

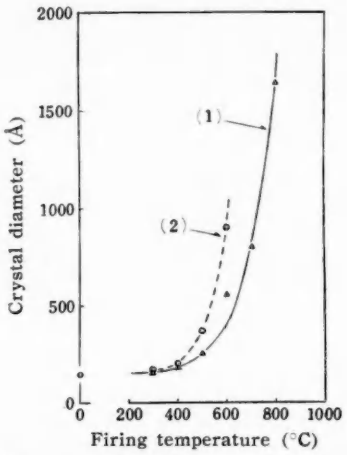


Fig. 3. Relationship between the firing temperature and the diameter of crystals;
(1) without flux, (2) with added 2 wt. % NaCl as flux.

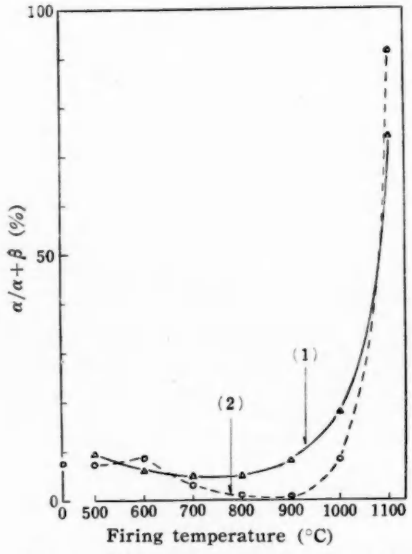


Fig. 4. Relationship between the firing temperature and the crystal form of ZnS: Ag phosphor;
(1) without flux, (2) with 2 wt.% NaCl as flux.

is about 0.2 μ. This is also true for the sample fired by 600°C. However, for the sample fired at 600°C with flux, as shown in Fig. 2a, the diameter is 0.1 μ from X-ray diffraction and is 0.3~0.4 μ from the electron microscope experiment. The disagreement is probably due to the growth of thin plate-like crystals under this particular condition.

Relationship between the Firing Temperature and the Crystal Forms.—The transition of the crystal forms of zinc sulfide takes place at about 1020°C[6]. It is known that, below 1050°C, the β-form is stable and, above 1100°C, the hexagonal α-form is stable[7]. However, from our experiments the situation seems to be a little more complicated.

In Fig. 4, the ratio of the amount of α-form to that of β-form in crystal was given, which was obtained by comparing the strengths of the strongest diffraction patterns, $10\bar{1}0$, 0002 and $10\bar{1}1$ of α-form, with that of β-form, 111. The measurements were made for zinc sulfide phosphors fired for three hours at various temperatures ranging from 500°C to 1100°C, with the raw material containing 8% of α-form.

As is seen in Fig. 4, the amount of α-from in the material without flux decreases as the firing temperature increases, and the transition from α-from to β-form is observed. However, at about 900°C, the content of α-form begins to increase again and becomes 18% at 1000°C and 73% at 1100°C. For the sample with the flux of 2 wt. % of sodium chloride, the α-form begins to decrease at about 700°C. Almost all of the α-form changes into β-form at 800°C, and the amount of α-form becomes nearly equal to zero. As the temperature increases, the α-form appears again at about 1000°C and more than 90% of α-form is found at 1100°C.

The above results show the fact that the transition velocity of crystal forms is much influenced by the existence of the flux and that the transition, α-form $\leftrightarrow$ β-form, becomes easier with 2 wt. % of sodium chloride, but is difficult without it.

The increase of α-form is observed at 600°C for the sample with 2 wt. % of sodium chloride, but the same phenomenon appears in the cases with fluxes other than sodium chloride. The explanation of this is not given yet, and the author is planning to check whether it originates from the existence of some meta-stable state which promotes the formation of α-state, because of some critical temperature to stimulate the sudden crystallization, or whether it is due to the existence of a

6) E. T. Allen and J. L. Crenshaw, *Am. J. Science*, **34**, 341 (1912).
7) R. H. Bube, *J. Chem. Phys.*, **20**, 708 (1952).

state where the α-form is essentially stable.

Influence of Time of Firing.—Fig. 5 gives the relationships among the time of firing, the crystal forms and the intensity of luminescence. At firing temperature of 1000°C, there is not much difference in crystal forms between the sample fired for ten minutes and that fired for three hours, and the former shows a considerably better luminescence intensity. This fact implies that the crystallization has taken place during the firing for a short period. At firing temperature of 800°C, the amount of α-form decreases with the time of firing and the greater part of the crystals are of β-form after firing for thirty minutes. The intensity of luminescence shows a similar tendency and attains the limiting value in thirty minutes.

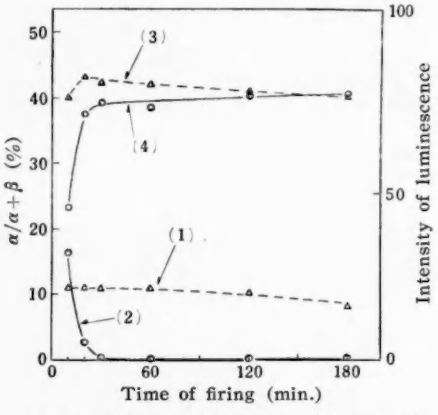


Fig. 5. Relationships among the time of firing, the crystal forms and the intensity of luminescence.
(ZnS: Ag added 2 wt. % NaCl as flux.)
(1) Content of α-form (fired at 1000°C).
(2) Content of α-form (fired at 800°C).
(3) Intensity of luminescence (fired at 1000°C; 12 kV. C.R. excitation).
(4) Intensity of luminescence (fired at 800°C; 12 kV. C.R. excitation).

Those facts imply that the complete change from α-form into β-form is finished within ten minutes when fired at 1000°C and after thirty minutes when fired at 800°C, both with 2 wt.% of sodium chloride as flux.

Summary

(1) The zinc sulfide, before firing, is a large aggregate of crystallites with the crystal diameter of about 150 Å and contains about 8% of α-form.

(2) The crystal growth of zinc sulfide phosphor takes place at about 500°C regardless of whether there is flux or not, but the rate of the growth is much affected by the flux. Without flux, the crystal grows as step-wise piled layers, but, with flux, it grows isotropically showing no influence from the crystal symmetry. Concerning the above difference, there has been discussion, taking into account the density of kinks at the step-wise surfaces of crystals and the change of diffusion constant of zinc sulfide molecules adsorbed at the surfaces.

(3) The transition, α-form $\leftrightarrow$ β-form, of zinc sulfide phosphor is rather easy, but becomes difficult without flux. Also, the transition is completed in thirty minutes of firing at 800°C with the flux of 2 wt.% of sodium chloride, but it is completed within ten minutes of firing at 1000°C.

(4) It is probable that there is a metastable state of α-form at about 600°C, but it requires further consideration.

The author wishes to express his thanks to Mr. T. Mitsuishi and Mr. H. Nagasaki for their cooperation in the X-ray diffraction measurements and the electron microscope experiments.

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Recombination of Hydrogen Atoms on Various Transition Metal Surfaces

By Kazuo NAKADA

(Received January 20, 1959)

Apart from the well-known research of Bonhoeffer[1], in which the order of recombination activity of metals was found to be in good accordance with the series of hydrogen over-voltage, comparison of the relative activities of various kinds of metals for the recombination of hydrogen atoms was made by Katz et al.[2] However, our present knowledge about the recombination activity of transition metals is not sufficient for the detailed discussion.

From the works just cited, it is immediately noticed that the transition metals have the highest activity among all sorts of metals, noble metals follow them, and polyvalent metals have much lower activity as compared with the former two. However, it is not yet well understood why such a distinct change in activity appears when metal species are altered, even though it might be inferred that different electronic band structures are responsible for the difference in activity.

In order to examine the dependence of recombination activity principally on the *d*-band hole, the comparison of activities was made for several transition metals available for us.

We further attempted to obtain the information about the correlation between the work function and the recombination coefficient, which had attracted our attention ever since Suhrmann[3] had made clear many years ago the linearity between them, for it seems to be open to question whether the exact linearity would hold over all kinds of metals at all.

Trapnell et al.[4] intended to interpret the origin of different activities in terms of the so-called Pauling's *d*-character. It is another aim of the present work to make clear in what manner the *d*-character can be related to the catalytic activity.

1) K. F. Bonhoeffer, *Z. physik. Chem.*, **113**, 199 (1924).
2) S. Katz, G. B. Kistiakowsky and R. F. Steiner, *J. Am. Chem. Soc.*, **71**, 2258 (1949).
3) R. Suhrmann and H. Csesch, *Z. physik. Chem.*, **B28**, 215 (1935).
4) K. G. Pickup and B. M. W. Trapnell, *J. Chem. Phys.*, **25**, 182 (1956).

Experimental

In order that the place where the recombination proceeds was confined to the metal surface concerned, a method adequate to be called "an effusion method" was adopted here instead of the usual flow method.

The relative activities of Ta, W, Mo, Ti, Co and Cr were determined with respect to Ni. In the series of Fe, Cr, Mn and Cu, Cu was chosen as a standard of comparison. In another series of Ti, Zr and Th, Ti was adopted as a standard metal. U was compared only with Mo.

Samples.—Most metal samples used were in the form of a circular disk (15 or 20 mm. in diameter and 0.1~0.3 mm. thick), but Ti and Zr were ribbon-like foil. Fe and Mn were electrically plated on one side of copper plate, while Cr was evaporated on copper plate in a vacuum.

Two kinds of metals, one of which was chosen as the standard metal, were stuck together back to back by soldering or spot welding or, in unavoidable cases, by means of synthetic resin adhesives. Their surfaces were polished with 06 emery papers, but no other treatment like chemical etching or electropolishing was done at all.

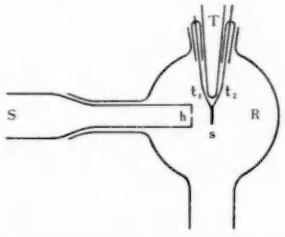

Fig. 1. Main part of apparatus.
S: The side tube of discharge tube
R: The reaction chamber
h: A small circular hole
t_1, t_2: Pt/Pt−Rh thermocouple
s: The sample
T: The top tube inside of which the city water was allowed to flow.

Apparatus and Procedure.—Only the main part of apparatus, made of hard glass, was shown in Fig. 1. Hydrogen atoms were produced in a Wood's discharge tube. The electric discharge was carried out by an alternating current from 5 kW. transformer giving up to 4000 V. The voltage across the electrodes was of the order of 1000~1500 V.

The hydrogen gas including hydrogen atoms was allowed to effuse into the reaction chamber (B) through a small circular hole (h) provided at the end of the side tube (S). In this chamber the sample metal disk was hung by molybdenum wire (0.3 mm. in diameter) at the front of the hole. This chamber was strongly pumped off by an oil diffusion pump backed by a rotary oil pump, but could not be evacuated to less than 5×10^{-4} mmHg on account of leakage gas from the hole.

Even such a non-high vacuum seems to be sufficiently good to ensure that the reaction gas reaches the catalyzing metal surface not by diffusion but rather by effusion, considering the much shorter distance between the sample surface and the hole than the mean free path at the vacuum of 10^{-3} mmHg.

The temperature rise of the sample caused by recombination heat liberating on it was followed by measuring the electromotive force of Pt/Pt-Rh thermocouple attached to the sample by use of a K-type potentiometer. The sample metal disk could be allowed to turn over by virtue of the ground glass joint. Inside the tube (T), in the bottom of which molybdenum lead was sealed, the city water was allowed to flow in order to diminish the effect of the drift of room temperature on the measurements. This procedure was useful to eliminate the error resulting from temperature variation, because the drift of city water temperature was smaller than that of room temperature by a factor of about 5.

Hydrogen. — Commercial cylinder hydrogen was used. The gas was allowed to bubble through a saturated solution of sodium hydroxide. After being dried with sulfuric acid, it was passed over the platinized asbestos (ca. 400°C), and dried again over the phosphoric pentoxide. Hydrogen thus dried was sent to 3 l. flask equipped with a manostat capable of keeping the pressure constant within 0.1 mmHg.

Hydrogen was allowed to diffuse into the discharge tube through a capillary. At this stage the pressure was lowered enough to permit the electric discharge.

In order to keep the catalytic action of discharge tube wall as constant as possible, hydrogen at a pressure of about 150 mmHg was saturated with water vapour on the saturated solution of sodium hydroxide.

Result. — The electromotive forces of two thermocouples, one of which was attached to the sample and the other was immersed in a city-water stream, was read simultaneously for the intervals of 5 min. over the range of 1 to 2 hr. before and during the course of electric discharge. The values averaged over all the reads are taken as expressing the temperatures of the sample and the city-water. The difference of these temperatures varied before and after the discharge was switched on. This variation of temperature difference was adopted as the rise of temperature due to the recombination heat.

At first the temperature rise for the metal aimed at was determined, then the same procedure was applied to the standard metal of another side. The ratio of the former to the latter was adopted as a measure of the recombination coefficient. The values thus determined were summarized as follows:

a) for the case when nickel was adopted as a standard metal, Co(118), Ni(100), Ta(88), Mo(86), W(84), Ti(83) and Cr(71):

b) for the case when copper was a standard metal, Fe(167), Cr(120), Mn(111) and Cu(100).

The latter case could be converted into the former case as given below:

Fe(99), Cr(71), Mn(66), and Cu(59).

In the series of Ti, Zr and Th, the order of activity was determined as follows:

$$Zr>Ti>Th$$

From the comparison of U with Mo, the relation

$$Mo>U$$

was obtained.

Discussion

In this section, present results have been discussed from several points of view through comparison of activity with physical properties. At first we confine ourselves to metals belonging to the first long period of the periodic table.

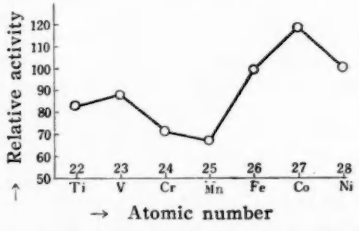

Fig. 2. The dependence of relative activity on atomic number, where Ta is taken in place of V.

In Fig. 2 is given the dependence of the recombination activity on atomic number, where tantalum is used in place of vanadium. It is perceived that this plot has two peaks at group V and group VIII. On the other hand, if the cohesive energy[5] is plotted against the atomic number, Fig. 3 curve a is obtained. It is noticed that this plot has also two peaks at the same positions. When other physical properties, e.g., the effective electron number per atom[6], density of states per eV. per atom[7], etc., are plotted against the atomic number, plots similar to the above are obtained as shown in Fig. 3 curve b. From the resemblance of these plots to the plot in

5) C. Kittel, "Introduction to Solid State Physics", John Wiley & Sons, New York (1956), p. 99.
6) Ibid., p. 132.
7) Ibid., p. 259.

Fig. 2, it is suggested that these physical properties are more or less related to the catalytic activity.

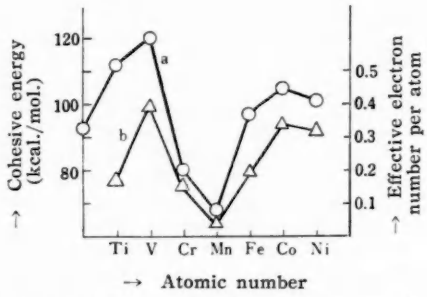

Fig. 3. Curve a, plot of cohesive energies versus the atomic number and curve b, plot of the effective electron number versus the same.

Let us consider a little further the correlation of activity with the cohesive energy. From the resemblance between the plot of cohesive energy versus the atomic number and that of activity versus the same, it is suggested that the bond strength of chemisorption which can be evaluated by an approximate method stated just below, may have an important connection with the catalytic activity. Recently, a method for evaluating the bond strength of chemisorption approximately by use of the experimental heat of sublimation and the electronegativity had been presented by Eley[8]. More recently, a somewhat different method was offered by Stevenson[9], in which the work function was used instead of the value of dipole moment in evaluating the ionic contribution.

If the semi-empirical values of bond strength of chemisorption evaluated by the above two kinds of methods are taken, plots quite similar to the relation between cohesive energy and atomic number must be obtained. From this fact, the conclusion may be drawn that metals having strong bond strength of chemisorption should have high activity. However, the statement given below has made such a view less convincing.

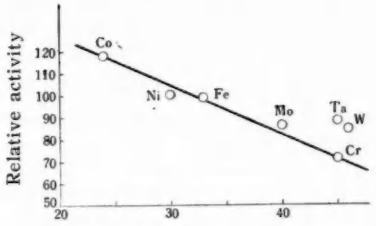

Fig. 4. The dependence of the relative activity on the experimental heat of chemisorption, where the data are taken from Stevenson's report.

Alternatively, if the recombination activities are plotted against the data on the experimental heat of chemisorption quoted by Stevenson, it is found that almost all points fall on a straight line aside from the slight upward deviation of tantalum and tungsten as shown in Fig. 4. From this fact, it is suggested that metals with strong bond strength of chemisorption are less active in contrast to the above statement deduced from the comparison of the dependence of cohesive energy on atomic number with that of activity on the same.

In order for the surface recombination to proceed, if the Rideal mechanism is assumed, hydrogen atoms need be chemisorbed first on bare metal surface and yet their bonds must have moderate strength to be ready to break on the attack of a chemisorbed layer by hydrogen atoms from the gas phase so as to reproduce hydrogen molecules, for it is supposed that the activation energy for the latter process can be approximated to be proportional to the chemisorption bond strength[10].

Obviously, the reason why polyvalent metals have low activity comes from the fact that the Brillouin zone is almost fully filled and, accordingly, only a few sites can be used for hydrogen atom chemisorption. On the contrary, in the case of transition metals with unfilled *d*-orbitals capable of supplying ample sites for the appreciable adsorption to occur, it seems likely that the bond strength of chemisorption may play a more important role in

8) D. D. Eley, *Discussions Faraday Soc.*, **8**, 34 (1950).

9) D. R. Stevenson, *J. Chem. Phys.*, **23**, 203 (1955).
The surface M-H bond can be calculated from Pauling's equation
$E(\mathrm{M-H})=1/2\{E(\mathrm{M-M})+E(\mathrm{H-H})\}+23.06(x_{\mathrm{M}}-x_{\mathrm{H}})^2$
where $E(\mathrm{M-M})$ is one sixth of the experimental sublimation energy and $E(\mathrm{H-H})$ is the dissociation energy of hydrogen molecule. The difference of electronegativity, $x_{\mathrm{M}}-x_{\mathrm{H}}$, can be approximated as equal to the dipole moment of the bond in debyes, the values of which are known from the data on contact potential.

10) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Process", McGraw-Hill Book Co., New York (1941), p. 152.
In the three-atom reaction AB+C→A+BC, the activation energy can be approximated to be 0.055D', where D' is the dissociation energy plus zero point energy of AB molecule.

determining the catalytic activity than the number of sites. The correlation between the experimental heat of chemisorption and recombination activity may be understood, in a sense, in terms of different bond strength of chemisorption.

Even though it is not known at what degree of coverage recombination would proceed in the present experimental condition, the above slight deviation in the case of tantalum and tungsten might be attributed in part to such a character of adsorption as that when the heat of chemisorption of hydrogen on them decreases more markedly with increasing coverage than the case of nickel and iron[11].

However, there seems to be another explanation of the origin of low activities of some transition metals (e.g., Ti, Zr and Th). The transition metals can be grouped into two main classes[12], because of wide diversity of their behavior for hydrogen absorption. Namely, metals of group A absorb hydrogen endothermically and those of group B exothermically. As a whole, it is permissible to say that the former just corresponds to the more active group, and the latter to the less active group. Though it is not clear to what extent the parallelism between hydrogen absorption and adsorption would be preserved, some kinds of resemblance between them may be excepted to exist concerning the state of hydrogen atoms in and on metals. With this in mind, the different activities of group A and B metals can be explained in the following way: In the case of group B metals a hydride layer on which hydrogen atoms are adsorbed with difficulty, would be formed. Contrary to this, in the case of group A the usual monoatomic chemisorbed layer of hydrogen is formed serving as the intermediate compound of this recombination reaction.

Next, let us examine how the physical properties, e.g., work function, *d*-character and surface potential of chemisorbed hydrogen atom layer, may correlate to recombination activity.

In view of Suhrmann's old work it is permissible to say that the larger the work function, the higher the activity. As shown in Fig. 5 curve a, the values of work function[13] of the first long period metals show a tendency to increase with

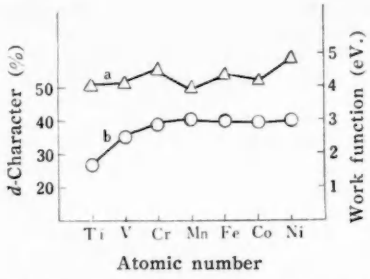

Fig. 5. Curve a, plot of the work function versus the atomic number and curve b, plot of the *d*-character versus the same.

the atomic number, despite the existence of rather complex ups and downs. Such a tendency as that where both catalytic activity and work function increase with the atomic number seems to support Suhrmann's view in the limited sense. However, this view may be, if anhything, an approximation, considering the fact that with respect to recombination activity, for example, the relation Ni<Co, Ti<Zr, and W<Mo was obtained by the present author, while the opposite relation holds for the work function.

Trapnell et al.[14] predicted that the *d*-character, which was defined by Pauling, might play an important role in the present reaction. From the present author's result it can be said that metals with large *d*-character have, on the whole, high activity. However, the monotonous increase of *d*-character with atomic number, as shown in Fig. 5 curve b is not adequate to explain the existence of two peaks in the activity-atomic number plot.

So long as the data[15] available up to date are concerned, metals can be roughly classified into two groups according to the magnitude of the absolute values of surface potential of chemisorbed hydrogen layer. The first group metals corresponding to the higher value, to which W (−0.48 or −0.65 V.) and Ta (−0.9, −1.2 or −0.43 V.) belong, have lower activity than the second corresponding to the lower value, to which Fe (−0.19 or −0.47 V.), Ni (−0.1 or −0.12 V.) and Co (0.06 V.) belong. This is naturally accepted from the statement given before, considering the fact that metals corresponding to large surface potential values have generally large experimental chemisorption heats. Accordingly, there seems to be no direct connection between

11) O. Beeck, *Discussions Faraday Soc.*, **8**, 118 (1950).
12) S. Dushman "Scientific Foundation of Vacuum Techniques", John Wiley & Sons, New York (1949), p. 553.
13) H. B. Michaelson, *J. Appl. Phys.*, **21**, 536 (1950).
14) Loc. cit.
15) J. J. Broeder, L. L. van Reijen, W. M. H. Sachtler and G. C. A. Schuit, *Z. Elektrochem.*, **60**, 838 (1956).

the degree of polarization of chemisorbed hydrogen atom and recombination activity.

Our attempt to explain the different recombination activities in terms of any one of physical properties proves less successful. This is probably because there is no strict theory capable of connecting the activity to the physical properties. At any rate, it is apparent that many more quantitative experiments remain to be done before a systematic account can be given concerning the origin of different activities of transition metals for this recombination reaction.

Summary

A study has been made of surface recombination of hydrogen atoms on various transition metals.

Hydrogen atoms were produced in the electric discharge tube by use of an alternating current. In order to prevent the reacting gas from reaching the undesired part of the sample, a method which may be called "an effusion method" was adopted here. The relative activity of two kinds of metal plates, stuck together by the solder or some such material, was determined, comparing the temperature rises of the sample by means of alternative exposure of each side surface to the reacting gas.

The following results were obtained:

a) Co> Fe> Ni> Ta> Mo> W> Ti> Cr > Mn> Cu

b) Zr> Ti> Th

c) Mo> U

These orders of activity were examined from several points of view through the comparison of recombination activity with the work function, the *d*-character, the experimental heat of chemisorption, etc.

The present results are still fragmentary but may suffice to show a qualitative trend.

The author wishes to express his gratitude to Professor S. Shida for his kind encouragement and to Mr. I. Yasumori for his helpful advice.

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On the Reactivity of Amide Group of ε-Caprolactam Derivatives

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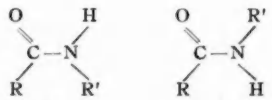
(Received January 28, 1959)

The bond between carbon and nitrogen of an amide has appreciably double bond character due to resonance[1], and the configuration of amide linkage tends to be a planer structure and two configurations of *cis* and *trans* forms are possible as follows:



cis form *trans* form

ε-Caprolactam is the *cis* form[2], while monosubstituted acid amide RNHCOR′ is the *trans* form[3]. It was ascertained[4] that ε-caprolactam caused an amide interchange reaction with a *trans* amide and the reaction rate of ε-caprolactam with its ring oligomers became faster with the enlargement of the ring. When it is compared with the polymerization of ε-caprolactam, the equilibrium between ring and chain structures shifts to the ring form in the case of the polymerization of substituted ε-caprolactam such as γ-methyl-ε-caprolactam, and *N*-methyl-ε-caprolactam is too stable to polymerize[5]. Therefore, this study was undertaken in order to elucidate the difference in reactivity of amide group of ε-caprolactam derivatives.

1) G. W. Wheland, "Resonance in Organic Chemistry", John Wiley & Sons, Inc., New York (1955), p. 109.
2) M. Tsuboi, This Bulletin, **22**, 215 (1949).
3) S. Mizushima et al., *J. Am. Chem. Soc.*, **72**, 3490 (1950).
4) N. Ogata, Contributed to the *Makromoleculare Chemie*.
5) H. Yumoto, K. Ida and N. Ogata, This Bulletin, **31**, 249 (1958).

Experimental

1. Determination of the Dipole Moment of Amides.—The dipole moment of ε-caprolactam, γ-methyl-ε-caprolactam and *N*-methyl-ε-caprolactam was determined in benzene solution at 25°C, as shown in Table I. The molecular polarization of ε-caprolactam or γ-methyl-ε-caprolactam decreased with the increase of the concentration but that of *N*-methyl-ε-caprolactam was almost constant, as shown in Fig. 1.

TABLE I. THE DIPOLE MOMENT OF ε-CAPROLACTAM DERIVATIVES

Sample	Dipole moment (D)
ε-Caprolactam	3.88
γ-Methyl-ε-caprolactam	5.48
N-Methyl-ε-caprolactam	4.23

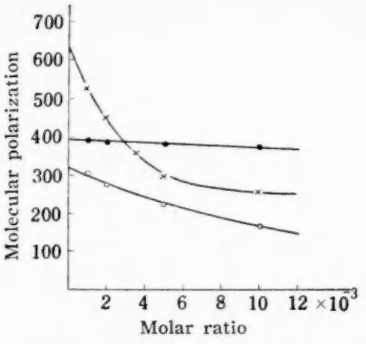


Fig. 1. The molecular polarization of ε-caprolactam derivatives.
● *N*-Methyl-ε-caprolactam
× γ-Methyl-ε-caprolactam
○ ε-Caprolactam

TABLE II. THE RATE OF HYDROLYSIS OF ε-CAPROLACTAM

Temp. (°C)	Concn. of H_2SO_4 (N)	Reaction time (hr.) 1/6	1/3	1/2	1	2	3	5	7	8
60	1.0	—%	—%	—%	4.9%	6.7%	11.4%	15.1%	21.2%	—%
60	2.0	—	—	—	8.2	12.9	19.4	32.7	42.9	—
80	1.0	—	—	13.1	21.0	34.7	43.3	59.5	67.1	—
80	2.0	10.9	15.0	16.0	38.0	56.9	78.9	88.0	—	—
100	0.5	—	—	24.9	40.8	49.2	56.1	63.3	—	—
100	1.0	21.7	32.9	44.9	66.3	87.3	93.2	97.5	—	100.0
100	1.5	28.2	56.8	60.2	80.6	100.0	—	—	—	—
100	2.0	35.3	60.2	64.7	86.5	100.0	—	—	—	—

TABLE III. THE RATE OF HYDROLYSIS OF RING OLIGOMERS
(Concentration of sulfuric acid, 3 N)

Ring oligomer	Temp. (°C)	Reaction time (hr.) 2	4	6	8	10	15	20
dimer	78	—%	—%	—%	5.2%	—%	8.8%	12.0%
	100	—	6.8	9.7	—	21.6	29.6	25.5
trimer	78	—	6.1	8.4	12.4	—	—	—
	100	18.0	32.0	38.0	42.3	—	—	—
tetramer	78	—	5.4	7.7	11.9	—	—	—
	100	20.0	28.5	34.0	39.0	—	—	—

TABLE IV. THE RATE OF HYDROLYSIS OF *N*-METHYL-ε-CAPROLACTAM

Temp. (°C)	Concn. of H_2SO_4 (N)	Reaction time (hr.) 1	2	3	4	5	7.5	10	15	20	30
80	3.0	1.8%	4.4%	6.3%	—%	12.9%	15.5%	18.5%	—%	—%	—%
90	3.0	—	10.2	—	17.2	21.7	31.5	40.1	—	—	—
100	1.0	9.4	16.0	19.7	24.0	27.6	—	40.3	—	—	—
100	2.0	10.8	18.0	27.4	34.9	40.5	—	60.8	—	—	—
100	3.0	12.3	23.5	30.3	36.5	43.9	57.6	67.9	75.8	82.2	89.8
100	5.0	8.4	18.0	26.1	38.6	46.7	—	100.0	—	—	—

2. Determination of the Reaction Rate of Hydrolysis.—ε-Caprolactam, *N*-methyl-ε-caprolactam or ring oligomers of ε-caprolactam which were obtained by repeated recrystallizations of the water extract of poly-ε-capramide, at the amount of 10^{-2} mol., was heated in 20 ml. of sulfuric acid in sealed glass tubes and then the solution was neutralized quickly. The quantities of ε-aminocaproic acid formed in the case of ε-caprolactam or its ring oligomers could be determined by the formol titration method but the quantitative determination of *N*-methyl-ε-aminocaproic acid was possible by neither the formol titration nor the method using an ion exchange resin. *N*-methyl-ε-aminocaproic acid could be quantitatively determined in the mixed solvent of ethanol and 30% formalin (1:1). The neutralized solution of *N*-methyl-ε-aminocaproic acid was filled up to 50 ml. and 10 ml. of the solution were dried and then the residue was dissolved in 10 ml. of ethanol and 30% formalin. The solution was titrated by 0.1 N sodium hydroxide solution with phenolphthalein as an indicator. These results are shown in Tables II, III and IV.

The hydrolysis of lactam in the presence of large quantities of water is the first order reaction and the rate constant is calculated by the following equation, where a designates the mole of amide and x the mole of amino acid formed at t hr.

$$k=2.303/t\cdot\log a/(a-x) \qquad (1)$$

The rate constants, which are shown in Table V, are proportional to the concentration of sulfuric acid, as shown in Figs. 2 and 3.

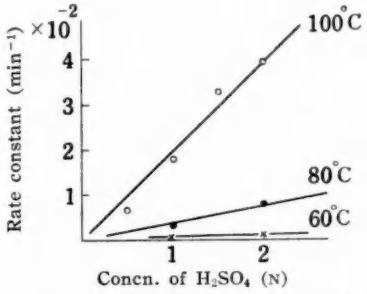


Fig. 2. The rate constant of hydrolysis of ε-caprolactam.

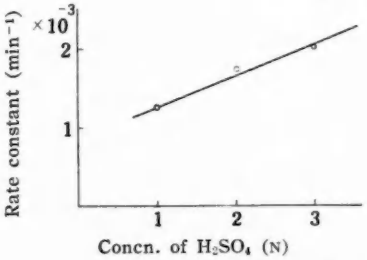


Fig. 3. The rate constant of hydrolysis of *N*-methyl-ε-caprolactam at 100°C.

TABLE V. THE RATE CONSTANT OF HYDROLYSIS OF ε-CAPROLACTAM DERIVATIVES

Sample	Temp. (°C)	Concentration of H_2SO_4 (N)	Rate constant (min^{-1})
ε-Caprolactam	60	1.0	0.6×10^{-3}
		2.0	1.3×10^{-3}
	80	1.0	3.5×10^{-3}
		2.0	8.0×10^{-3}
	100	0.5	6.4×10^{-3}
		1.0	18.1×10^{-3}
		1.5	33.2×10^{-3}
		2.0	39.4×10^{-3}
N-Methyl-ε-caprolactam	80	3.0	0.38×10^{-3}
	90	3.0	0.84×10^{-3}
	100	1.0	1.23×10^{-3}
		2.0	1.73×10^{-3}
		3.0	2.00×10^{-3}
Ring dimer	78	3.0	0.11×10^{-3}
	100	3.0	0.25×10^{-3}
Ring trimer	78	3.0	0.26×10^{-3}
	100	3.0	1.15×10^{-3}
Ring tetramer	78	3.0	2.33×10^{-3}
	100	3.0	13.75×10^{-3}

3. Determination of Infrared Spectrum.—The infrared spectrum of ε-caprolactam, ring-dimer, -trimer and -tetramer, which is shown in Figs. 4, 5, 6 and 7, was measured in a potassium bromide disc with a Hitachi model EPI-2 spectrophotometer, with a rock-salt prism. The absorption band of N-H of ε-caprolactam appears at 3215 and 3077 cm^{-1}, while that of ring-dimer at 3279 and 3077 cm^{-1}. The absorption band of CO of ε-caprolactam appears at 1650 cm^{-1}, while that of ring-dimer at 1639 cm^{-1}. The spectrum of ring-dimer shows absorption maximum at 1555 cm^{-1}, which is not found in ε-caprolactam. The absorption bands of N-H of ring-trimer and -tetramer appear at 3289 and 3077 cm^{-1} and the spectra come to resemble that of poly-ε-capramide (Fig. 8).

When dry hydrogen chloride was introduced into carbon tetrachloride solution of ε-caprolactam, a white crystal was precipitated. This crystal was decomposed easily in the air, evolving hydrogen chloride. It was filtered off in dry hydrogen chloride atomosphere and dried, and then its infrared spectrum was measured, in a potassium bromide disc, which is shown in Fig. 9. The absorption bands of N-H at 3215 and 3077 cm^{-1} disappear and new ones appear at 2730, 2500 and 2398 cm^{-1}. The absorption band of N-H of dibutylamine $(C_4H_9)_2N$-H appears only at 3311 cm^{-1}, while that of its hydrochloride at 2564, 2463 and 2398 cm^{-1}. Therefore, these new bands are estimated to be the absorption of N-H of the reaction product which was produced by adding hydrogen chloride to the nitrogen atom of ε-caprolactam. The absorption band of CO of the

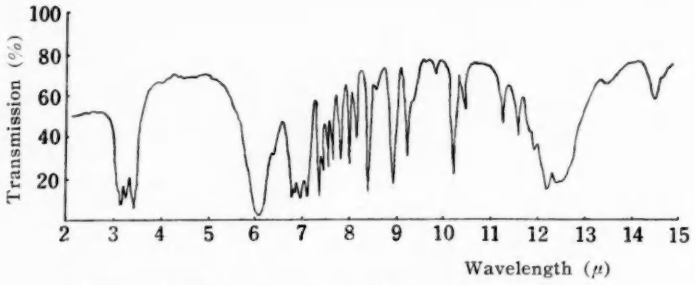


Fig. 4. The infrared spectrum of ε-caprolactam (KBr disc).

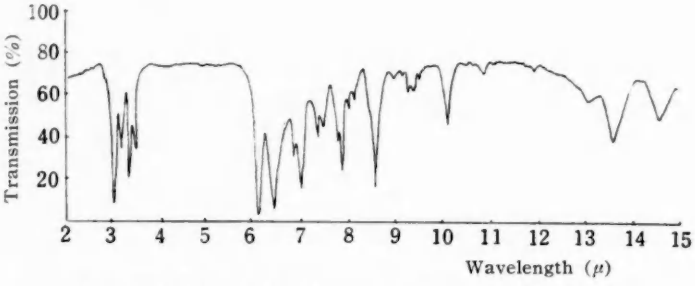


Fig. 5. The infrared spectrum of ring dimer (KBr disc).

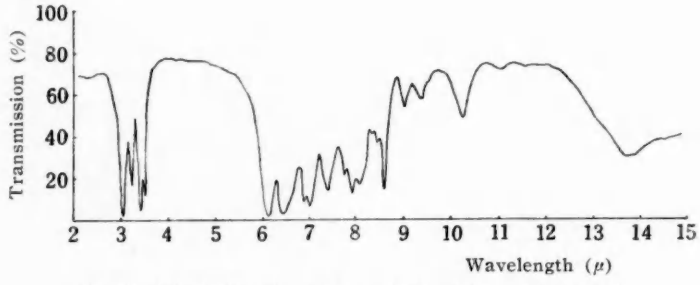


Fig. 6. The infrared spectrum of ring trimer (KBr disc).

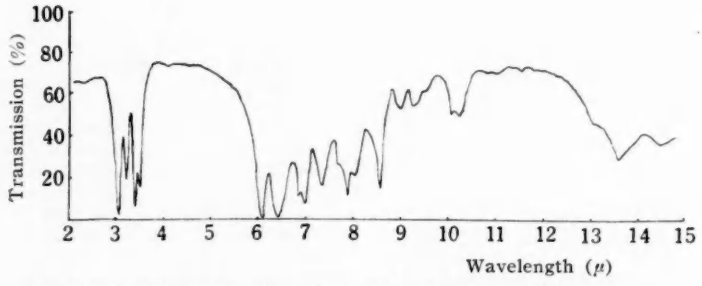


Fig. 7. The infrared spectrum of ring tetramer (KBr disc).

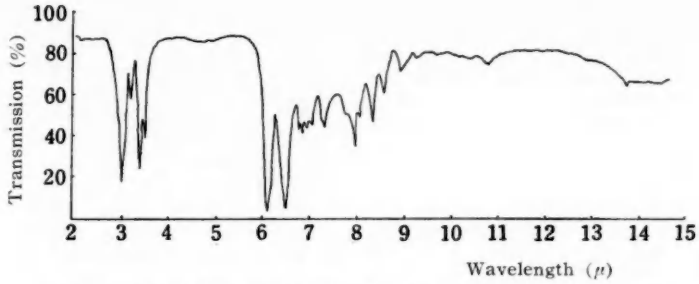


Fig. 8. The infrared spectrum of poly-ε-capramide (KBr disc).

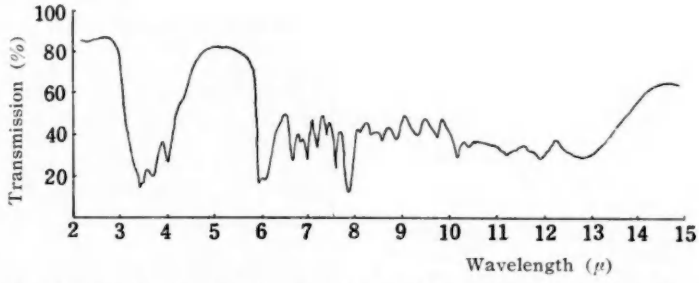


Fig. 9. The infrared spectrum of the reaction product of ε-caprolactam with hydrogen chloride (KBr disc).

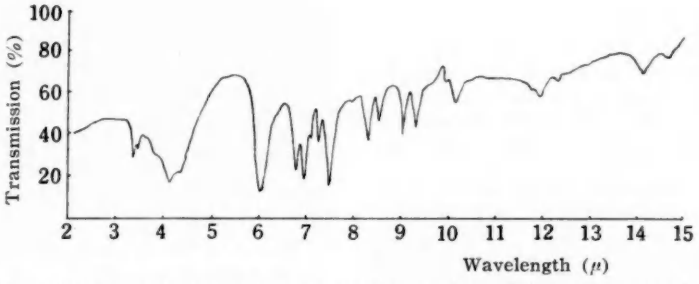


Fig. 10. The infrared spectrum of the reaction product of *N*-methyl-ε-caprolactam with hydrogen chloride (KBr disc).

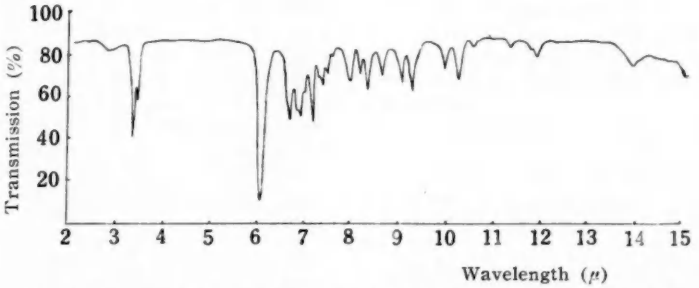


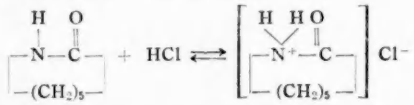
Fig. 11. The infrared spectrum of *N*-methyl-ε-caprolactam (liquid).

reaction product shifts from 1650 to 1681 cm^{-1}.

When dry hydrogen chloride was introduced into carbon tetrachloride solution of *N*-methyl-ε-caprolactam, a white crystal was precipitated but it dissolved again by the further introduction and *N*-methyl-ε-caprolactam was floated on carbon tetrachloride. The infrared spectrum of the crystal formed at first was measured in a potassium bromide disc, which is shown in Fig. 10. A new broad absorption appears at 2398 cm^{-1} which is tentatively assigned to the N-H band of the addition product of *N*-methyl-ε-caprolactam. The absorption band of CO of *N*-methyl-ε-caprolactam appears at 1645 cm^{-1}, which is shifted to the lower frequency than that of normal carbonyl compound, as shown in Fig. 11.

Discussion

ε-Caprolactam forms an addition compound with hydrogen chloride in carbon tetrachloride solution as follows



The ring opening reaction of ε-caprolactam in the presence of the ammonium cation[6] is presumed to be caused by the addition of the ammonium cation to the amide group.

The rate constant of hydrolysis of *N*-methyl-ε-caprolactam is about one twentieth of that of ε-caprolactam. The activation energy of hydrolysis of ε-caprolactam is calculated from the temperature dependence of the rate constants to be 20 kcal./mol., while that of *N*-methyl-ε-caprolactam 22 kcal./mol.

Since the molecular polarization of *N*-methyl-ε-caprolactam is almost constant with the increase of concentrations, it is expected that molecules do not associate at all. However, the absorption of CO in its infrared spectrum appears in much lower frequency than that of carbonyl compounds (about 1700 cm^{-1}). The dipole moment of *N*-methyl-ε-caprolactam is larger than that of ε-caprolactam.

From these results as stated above, it is expected that the amide linkage of *N*-methyl-ε-caprolactam has considerably ionic character due to resonance by the effect of methyl group as shown below and the stability of ring structure increases.

The rate constant of hydrolysis of ring-dimer is remarkably smaller than that of ε-caprolactam and that of ring-oligomers becomes faster as the ring becomes larger. It is ascertained[2,7] that the absorption of N-H of the *trans* or the *cis* amide appears in the 3370 to 3290 cm^{-1} or the 3240 to 3170 cm^{-1} regions in the infrared spectrum. The infrared spectrum of ring dimer, in the crystalline state, shows absorption maxima at 3279 and 3077 cm^{-1} and the configuration is expected to be not *cis*-[8] but *trans*- form. As the absorption band of CO of ring dimer appears in lower frequency than that of ε-caprolactam, ring-trimer or -tetramer, the low reactivity of ring dimer can be explained from the expectation that two amide groups are particularly favorable for the formation of two intramolecular hydrogen bonds and its structure is presumed to be as shown in Fig. 12. As amide groups lie too far apart to form the intramolecular hydrogen bond with the enlargement of the ring, the reactivity of ring oligomers becomes larger.

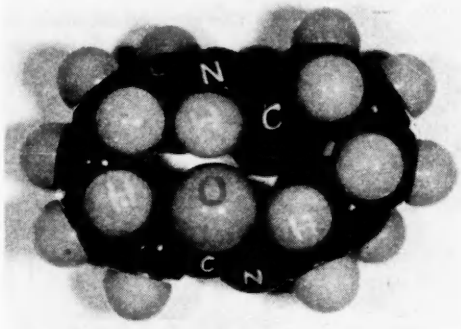


Fig. 12. The structure of ring dimer of ε-caprolactam.

Summary

The dipole moments, infrared spectra and rate constants of hydrolysis of ε-caprolactam derivatives have been determined in order to elucidate the difference in reactivity. The great stability of *N*-methyl-ε-caprolactam is expected, due to the increase of reasonance of amide linkage. Ring dimer of ε-caprolactam is stable for hydrolysis due to the strong intramolecular hydrogen bonds and the reactivity

6) H. Yumoto and N. Ogata, *Makromol. Chem.*, **25**, 71 (1958).
7) T. Miyazawa, T. Shimanouchi and S. Mizushima, *J. Chem. Phys.*, **24**, 408 (1950).
8) P. H. Hermans, *Nature*, **177**, 126 (1956).

of ring oligomers of ε-caprolactam increases as the ring becomes larger.

The author wishes to thank Dr. K. Hoshino and Dr. H. Kobayashi who instructed him in these studies and permitted the publication. He also thanks Mr. M. Nakata et al. who collaborated with him in experiments.

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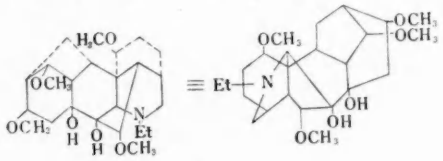
The Aconite Alkaloids. XXIX. Some Oxidation Products of Lycoctonine*

By Harusada SUGINOME, the late Shigehiko IMATO, Shozo YAMADA** and Nobukatsu KATSUI

(Received September 4, 1958)

The total structure of de-(hydroxymethylene)-lycoctonine (I) was determined by Przybylska and Marion[1] by X-ray crystallographic method, and that of lycoctonine (II) was proposed by Edwards, Marion and Stewart[2] on the basis of chemical evidences for the location of the hydroxymethylene group.



(I)

Fig. 1.

Most of the reactions and products have been interpreted[2,3] on the basis of these formulae; some of them are indicated in Fig. 2.

Since two new oxidation products from lycoctonine have been obtained, the present authors wish to report several arguments concerning their chemical properties and their relationship to other lycoctonine derivatives.

Oxidation of lycoctonam (III)[4] with chromic anhydride in N sulfuric acid solution gave three compounds, lycoctonamic acid (IV)[4], formic acid and a new neutral

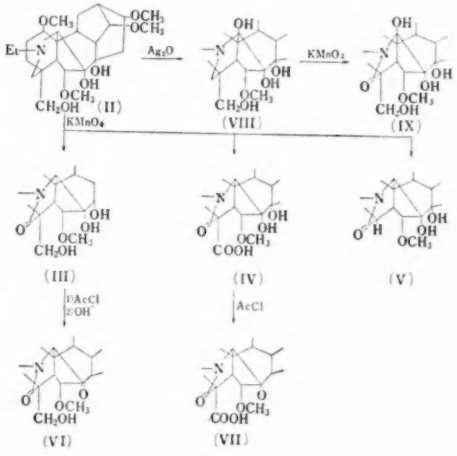
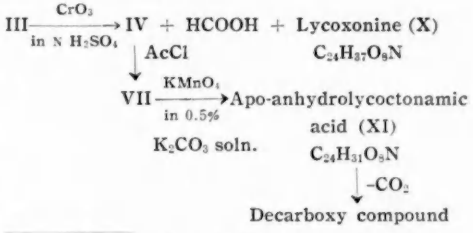


Fig. 2.

product, lycoxonine (X), $C_{24}H_{37}O_8N \cdot 4H_2O$, m. p. 80~83°C, $[\alpha]_D$ +40.8°.



* Part XXVIII, H. Suginome, N. Katsui and G. Hasegawa, This Bulletin, **32**, 604 (1959).

** Present address: Osaka Municipal Hygienic Laboratory, Kitaōgi-machi, Kita-ku, Osaka.

1) M. Przybylska and Léo Marion, *Can. J. Chem.*, **34**, 185 (1956).

2) O. E. Edwards, Léo Marion and D. K. R. Stewart, ibid., **34**, 1351 (1956).

3) O. E. Edwards, Léo Marion and K. H. Palmer, *J. Org. Chem.*, **24**, 1372 (1957).

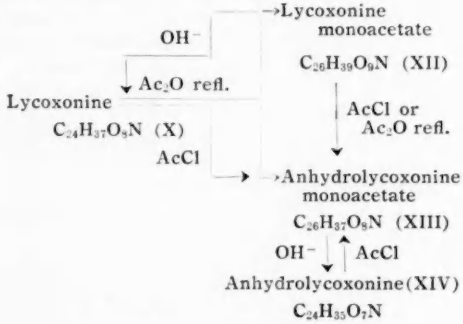
4) O. E. Edwards and Léo Marion, *Can. J. Chem.*, **30**, 627 (1952). These compounds had been isolated independently in these laboratories. (A report on them was read before the Annual Meeting of the Chemical Society of Japan, held in Tokyo, April, 1949, and the Meeting of the Hokkaido Branch of the Chemical Society of Japan, held in Sapporo, July, 1949). The names oxolycoctonine, L-acid and anhydro-L-acid were assigned for III, IV and VI, respectively.

On oxidation of anhydrolycoctonamic acid (VII)[4] with potassium permanganate in 0.5 per cent potassium carbonate solution, a new acid, apo-anhydrolycoctonamic acid (XI), $C_{24}H_{37}O_8N$, m. p. 183~184°C, $[\alpha]_D$ +37°, was yielded.

Lycoxonine (X) contains an *N*-ethyl and four methoxyl groups as does lycoctonam (III). In the infrared spectra of both compounds no decisive difference could be detected in the hydroxyl region because of the broad absorption. On the other hand, the bands due to lactam carbonyl were distinctly different (lycoxonine showed at 1631 cm^{-1} and lycoctonam at 1618 cm^{-1}). The same shift has been observed[4] between lycoctonam and the compounds in which the primary hydroxyl group has been acetylated or replaced by hydrogen. Since, from the above observations, the properties of the primary hydroxyl group were considered to be different, the acetylation of lycoxonine was examined.

Lycoxonine was acetylated with acetyl chloride at room temperature yielding anhydrolycoxonine monoacetate (XIII), m. p. 232~234°C, $[\alpha]_D$ +37.8°, or with acetic anhydride under reflux yielding the same anhydro monoacetate (XIII) and lycoxonine monoacetate (XII), m. p. 222~225°C. The compound XIII gave anhydrolycoxonine (XIV), m. p. 160~162°C, by hydrolysis.

However, lycoxonine is not acetylated on treatment with acetic anhydride and pyridine at room temperature, but lycoctonam (III) or other lycoctonine derivatives containing original the primary hydroxyl group have been readily acetylated[4] under the same conditions. Thus the formation of anhydro monoacetate (XIII) indicates the existence of the original glycol system and at least another hydroxyl group in lycoxonine (X). However, the hydroxyl group to be acetylated in lycoxonine is no longer the original primary one in view of the difficulty of acetylation.



This interpretation is in concordance not only with the properties of lycoxonine (whilst lycoctonam has been oxidized readily, lycoxonine is stable), but also with the observation of the infrared spectra of anhydrolycoxonine (XIV) and anhydrolycoctonam (VI) (the latter compound is derived from lycoctonam (III) by pinacolic dehydration). The absorption band at 3413 cm^{-1}, characteristic of the hydroxyl in compound VI, disappeared and a new band at 3534 cm^{-1} appeared in compound XIV. From the above results of acetylation, oxidation, and examination of spectra and compositions, it may be concluded that the properties of lycoxonine (X) are probably consistent with a structure in which the hydroxymethylene of lycoctonam (III) has been removed and a hydroxyl group has been produced.

It has been reported[2-4] that the substituent group, which is located at the bridgehead of the azabicyclo [3,3,1]-nonane system in the skeleton of lycoctonine, is readily removed. For example, de-(hydroxymethylene)-lycoctonam (V) has been formed during the permanganate oxidation of lycoctonine, and it has been obtained also by decarboxylation of lycoctonamic acid (IV). Thus, on the basis of the ready removal of the hydroxymethylene group, it may be considered that compound V is an intermediate in the formation of lycoxonine from lycoctonam. If this consideration is correct, the formation of formic acid during the oxidation will be explained by the analogous mechanism which has been suggested by Edwards, Marion and Stewart[2].

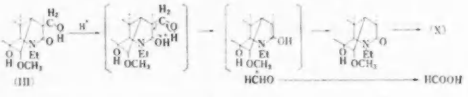


Fig. 3.

However, on the same treatment with chromic anhydride in N-sulfuric acid solution, de-(hydroxymethylene)-lycoctonam (V) is very stable against the reagents. On more vigorous treatment of lycoctonam (III) with the acid only, the hydroxymethylene group is left intact while lycoctonam undergoes extensive change[5]. It is, therefore, unlikely that de-(hydroxymethylene)-lycoctonam (V) is an intermediate. An attempt was made to determine the location of the new hydroxyl

5) O. E. Edwards, Léo Marion and R. A. McIvor, *Can. J. Chem.*, **32**, 708 (1954).

group, but decisive conclusions have not yet been obtained.

Recently an interesting compound, which may be related to the change from lycoctonam to lycoxonine, has been reported by Edwards, Marion and Stewart[2]. This compound was obtained by the action of lead tetraacetate on hydroxylycoctonam (VIII). It was suggested that it had a structure in which the hydroxymethylene group of compound VIII had been replaced by a new hydroxyl group and the glycol system had been cleaved.

Therefore, except for the cleavage of glycol, the properties of this compound appear to be closely analogous to those of lycoxonine. The same investigators[2] suggested in addition that it is difficult to demonstrate whether the skeleton of hydroxylycoctonine[6] (VIII) is or is not the same as that of lycoctonine. Hence, it is of interest to compare the action of chromic anhydride upon lycoctonam (lycoctonine skeleton) with that upon hydroxylycoctonam (hydroxylycoctonine skeleton), and to investigate whether the new hydroxyl group in lycoxonine is or is not located at the same position as that of the compound obtained by the above workers.

On treatment of hydroxylycoctonam (IX) with chromic anhydride in N sulfuric acid solution, two acids, Y-acid, m. p. 193~195°C, and C_I-acid, m. p. 220~222°C, and two neutral compounds, Y, m. p. 177~180°C, and Z, m. p. 226~227°C, were obtained. The properties of these compounds will be reported later.

The new acid, apo-anhydrolycoctonamic acid (XI), obtained by alkaline permanganate oxidation of anhydrolycoctonamic acid (VII), still contains an *N*-ethyl group. It shows the lactam band at 1597 cm^{-1} in the infrared spectrum, and gives a decarboxy-compound, m. p. 105~110°C. These evidences have been observed[4] analogously as in the case of the starting acid (VII), but the apo-acid (XI) contains only three methoxyl groups while the starting acid contains four.

In the ultraviolet spectrum the apo-acid (XI) shows the maximum at 305 mμ (log ε 2.07) which is usual in position but unusual in intensity; the maximum of dehydro-compounds from lycoctonine has been shown at 305 mμ (log ε 1.89). In addition, an oxime of the decarboxy-compound derived from the apo-acid shows the ultraviolet maximum still at 305 mμ, but the intensity is usual (log ε 1.85).

From the above observations, the conversion of anhydro-lycoctonamic acid (VII) to apo-anhydrolycoctonamic acid (XI) seems to involve the loss of one methoxyl and the formation of one carbonyl group. The detection of the produced carbonyl group was unsuccessful in the infrared spectrum, but the above consideration is supported by the chemical evidence that, whilst the starting acid VII is resistant to carbonyl reagents, the apo-acid consumes bromine quickly although the starting acid does not. The decarboxy compound from the apo-acid gave a 2,4-dinitrophenylhydrazone, m. p. 221~222°C, and an oxime, m. p. 140~142°C.

In the apo-acid (XI), the location of the removed methoxyl and the newly produced carbonyl group have not yet been determined. However, it is sure that the carbonyl group in anhydrolycoctonamic acid (VII) exerted some effects upon this conversion, because the analogous conversion was not observed in lycoctonamic acid (IV).

Experimental

Lycoctonam (III).—To a solution of 1 g. of lycoctonine in 70 cc. of acetone containing 7 cc. of water, was added 0.6 g. of powdered potassium permanganate in small quantities at room temperature; the resulting solution was left at room temperature overnight. After filtration of manganese dioxide, the filtrate was evaporated to syrup under reduced pressure. When the syrup was further concentrated in a desiccator, crystalline lycoctonam was separated. A further amount was deposited by the addition of ether. Thus 0.7 g. of crystal was obtained. This substance was recrystallized from ethyl acetate in needles, m. p. 95~98°C, $[\alpha]_D^{14}$ +67.5° (C, 1.10 in water).

Anal. Found: C, 58.05; H, 8.24; N, 2.74; H_2O, 6.94. Calcd. for $C_{25}H_{39}O_9N \cdot 2H_2O$: C, 58.01; H, 8.37; N, 2.71; H_2O, 6.96%.

In the infrared spectrum in Nujol, this compound showed broad bands at 3367, 3401 and 3460 cm^{-1} in the region of hydroxyl group. This compound was identical with lycoctonam, obtained in the same way as reported by Edwards and Marion[4].

Oxidation of Lycoctonam with Chromic Acid.—To a solution of 4 g. of lycoctonam in

6) It was reported in a previous paper[7] that hydroxylycoctonine was obtained from lycoctonine on oxidation with Ag_2O; Cookson and Trevett[8] reported that they had obtained also the same compound by means of lead tetraacetate. The present authors found that this compound was produced by treatment not only with the above reagents but also with potassium ferricyanide.

7) H. Suginome and K. Ohno, *J. Fac. Sci., Hokkaido Univ., Ser. III. Chem.*, **4**, 36 (1950).

8) R. C. Cookson and M. E. Trevett., *Chem. & Ind.*, **1956**, 276.

100 cc. of N sulfuric acid was added a solution of chromic anhydride in a small volume of water with ice-cooling. When the resulting solution was left at room temperature overnight, an acidic product a was separated in needles. After filtration of the acid a, the filtrate was extracted with chloroform. The chloroform extract containing the acidic and neutral materials was shaken with diluted aqueous ammonia. On evaporation the chloroform solution gave 1.15 g. of the neutral product, lycoxonine (see below).

When the aqueous ammonia layer was acidified with dilute sulfuric acid, an acidic product b was obtained. Thus the combined acidic product, a and b, weighed 1.45 g. After recrystallization from aqueous ethanol, this acid was confirmed to be identical with lycoctonamic acid (IV)[4], m. p. 200~203°C, after softening at 95~100°C, $[\alpha]_D^{15}$+94.2° (C, 1.66 in ethanol).

Estimation of Formic Acid Formed during Oxidation. — Lycoctonam was oxidized with chromic anhydride in the same way as described above. After being kept overnight, the major amount of the solution was distilled. When the distillate was just neutralized with 0.05 N sodium hydroxide and evaporated to dryness, crystals were obtained which decomposed at 250~253°C (authentic sodium formate decomposed at 255°C). The acidic material was confirmed to be formic acid by the chromotropic acid test after it was reduced to formaldehyde.

Lycoxonine (X).— This compound was obtained as described under oxidation of lycoctonam. It crystallized from water as a tetrahydrate in rhombic forms. After recrystallization it melted at 80~83°C and had $[\alpha]_D^{15}$+40.8° (C, 1.66 in ethanol). In the infrared spectrum in Nujol, lycoxonine showed the broad band at 3448 cm^{-1} in the region of hydroxyl group.

Anal. Found: C, 53.75; H, 8.48; H_2O, 13.52. Calcd. for $C_{24}H_{37}O_8N \cdot 4H_2O$: C, 53.42; H, 8.41; H_2O, 13.35%.

This compound was subjected to the Micro-Zeisel methoxyl, Herzig-Meyer *N*-alkyl and Ginger *C*-methyl[9] determinations.

Anal. Found: C_2H_5, 4.83; OCH_3, 23.20, CH_3, 2.45. Calcd. for $C_{18}H_{28}O_8N(CH_2 \cdot CH_3)(OCH_3)_4$: C_2H_5, 5.36; 4-OCH_3, 23.00; CH_3, 2.78%.

De-(hydroxymethylene)-lycoctonam (V).— Since this compound could not be isolated directly from the oxidation products of lycoctonine, the present authors obtained it by pyrolysis of lycoctonamic acid in the same manner as described in Edwards and Marion's report[4]. The compound obtained was recrystallized from water as a trihydrate, m. p. 110~113°C.

The melting point and the form of the trihydrate were not in agreement with the above report[4]. However, the derivatives of this compound, de-(hydroxymethylene)-lycoctonine perchlorate and anhydro-de-(hydromethylene)-lycoctonam, were well in agreement with those of the same report.

Upon subjection to the same treatment with chromic anhydride as described under oxidation of lycoctonam, this compound V did not react for more than three days.

Acetylation of Lycoxonine.— (i) Lycoxonine tetrahydrate (0.5 g) was treated with 2 cc. of acetyl chloride in a sealed tube at room temperature overnight. Excessive reagent was removed under reduced pressure, and water was added. On standing, the resulting aqueous mixture gave 0.2 g. of a crystalline product, anhydrolycoxonine monoacetate (XIII). It was recrystallized readily from ethanol in rosette forms, m. p. 225~230°C, $[\alpha]_D^{15}$+37.8° (C, 3.30 in ethanol). The ultraviolet absorption spectrum showed the maximum at 305 mμ (log ε 1.85).

Anal. Found: C, 63.38; H, 7.72; N, 2.67. Calcd. for $C_{24}H_{34}O_8N(OCOCH_3)$: C, 63.52; H, 7.59; N, 2.85%.

(ii) Anhydrous lycoxonine (0.1 g.), obtained by drying the hydrate under reduced pressure over phosphorous pentoxide, was treated with 1 cc. of acetic anhydride and 0.5 cc. of pyridine in a sealed tube at room temperature, but lycoxonine was recovered unchanged after more than 80 hr.

(iii) A solution of 0.5 g. of anhydrous lycoxonine in 0.7 g. of acetic anhydride was refluxed for 3 hr. and the solution was then concentrated to a syrup in a desiccator under reduced pressure. When a small amount of water was added to the resulting syrup, a crystalline product was obtained. This product could be separated into two parts by treating it with hot water. The first part was insoluble in hot water whilst the second was readily soluble. The insoluble material was identical with anhydrolycoxonine monoacetate which was obtained by acetyl chloride treatment (i). The readily soluble material was lycoxonine monoacetate (XII); it was recrystallized from water in prisms, m. p. 222~225°C.

Anal. Found: C, 61.35; H, 7.78; $OCOCH_3$, 10.43. Calcd. for $C_{24}H_{36}O_7 \cdot (OCOCH_3)$: C, 61.28; H, 7.71; $OCOCH_3$, 10.02%.

Lycoxonine monoacetate gave anhydrolycoxonine monoacetate upon further treatment with acetyl chloride or acetic anhydride as described above.

Anhydrolycoxonine (XIV).—Anhydrolycoxonine monoacetate was saponified by 50% potassium hydroxide in aqueous methanol on a steam bath for 30 min. The solution was neutralized with dilute hydrochloric acid and evaporated under reduced pressure to dryness. The resulting residue was extracted with ethanol. When the alcoholic solution was evaporated at room temperature, anhydrolycoxonine was separated in plates. After recrystallization from aqueous ethanol, it melted at 160~162°C and showed the maximum at 305 mμ (log ε 1.85) in ultraviolet spectrum.

Anal. Found: C, 64.38; H, 7.90; N, 3.21. Calcd. for $C_{24}H_{35}O_7N$: C, 64.12; H, 7.85; N, 3.12%.

Anhydrolycoctonamic Acid (VII).—Lycoctonamic acid (1 g.) was treated with 4 cc. of acetyl chloride in a sealed tube overnight. After evaporation of excess of the reagent, water was

9) L. G. Ginger, *J. Biol. Chem.*, **156**, 453 (1944).

added to the resulting residue. Then, 0.5 g. of an amorphous material was obtained, which crystallized readily from ethanol in prisms, m. p. 177~178°C, $[\alpha]_D^{13}$+52.8° (C, 1.00 in ethanol), λ_{max} 305 mμ (log ε 1.87). This product was identical with anhydrolycoctonamic acid reported by Edwards and Marion[4].

Anal. Found: C, 62.47; H, 7.38. Calcd. for $C_{25}H_{35}O_8N$: C, 62.87; H, 7.39%.

Apo-anhydrolycoctonamic Acid (XI).—To a solution of 0.5 g. of anhydrolycoctonamic acid in 100 cc. of water containing 0.5 g. of potassium carbonate, 0.3 g. of powdered potassium permanganate was added in portions at room temperature. The potassium permanganate was consumed very slowly in three days.

The manganese dioxide was filtered off and washed with 0.1% potassium carbonate solution. When the combined filtrate and washings were acidified with diluted sulfuric acid, apo-anhydrolycoctonamic acid was obtained. Yield, 0.19 g. It was recrystallized from ethanol in thin plates, m. p. 183~184°C, $[\alpha]_D^{13}$+37° (C, 1.00 in ethanol). This acid was considerably less soluble in ethanol than anhydrolycoctonamic acid. The ultraviolet spectrum of this acid showed the maximum at 305 mμ (log ε 2.07).

Anal. Found: C, 62.14; H, 6.69; OCH_3, 20.20. Calcd. for $C_{24}H_{31}O_8N$: C, 62.45; H, 6.77; 3-OCH_3, 20.17%.

On oxidation in the same way as described above, lycoctonamic acid was not affected.

The apo-acid decolorized one mole of bromine within 30 min. in acetic acid, while anhydrolycoctonamic acid did not do so within 24 hr.

Decarboxy Compound of Apo-anhydrolycoctonamic Acid.—(i) On treatment of apo-anhydrolycoctonamic acid in the same way as reported by Edwards and Marion[4], no crystalline product was isolated.

(ii) A solution of 40 mg. of the apo-acid in 0.3 cc. of acetic anhydride was refluxed for 3 hr. The solution was poured into 10 cc. of water, and the resulting aqueous solution was extracted with chloroform. After being washed with diluted potassium hydroxide and then with water, the chloroform extract was evaporated to dryness. When ether was added to the residue, crystals were deposited from the ether solution in prisms. The substance was recrystallized from water as a polyhydrate, which melted at 110~113°C after softening at 100°C.

Formation of Oxime and 2,4-Dinitrophenylhydrazone from the Decarboxy Compound.—(i) To a solution of 40 mg. of the decarboxy compound in 1 cc. of ethanol was added a solution of 40 mg. of hydroxyl amine hydrochloride in 0.4 cc. of water containing 40 mg. of potassium carbonate; the resulting solution was warmed on a steam bath for 4 hr. When the alcoholic solution was concentrated under reduced pressure, the oxime of the decarboxy compound was separated in needles, m. p. 140~142°C. In the ultraviolet spectrum, this oxime showed the maximum at 305 mμ (log ε 1.85).

Anal. Found: N, 6.54. Calcd. for $C_{23}H_{32}O_6ON$: N, 6.48%.

(ii) To a solution of 20 mg. of the decarboxy compound in 2 cc. of ethanol was added four drops of the solution of 0.5 g. of 2,4-dinitrophenylhydrazine and 1 cc. of 90% sulfuric acid in 7 cc. of ethanol. When the resulting solution was allowed to stand at room temperature for several hours, it deposited 2,4-dinitrophenylhydrazone of the decarboxy compound in yellow needles, m. p. 221~222°C.

Anal. Found: N, 11.54. Calcd. for $C_{29}H_{35}O_9N_5$: N, 11.72%.

On treatment of anhydro-de-(hydroxymethylene)-lycoctonam with either of the above reagents, the starting compound was recovered without change.

Hydroxylycoctonine (VIII).—A solution of lycoctonine in 20 cc. of methanol was mixed with a solution of 1.2 g. of potassium hydroxide in 20 cc. of methanol. Then, a solution of 5.4 g. of potassium ferricyanide in 25 cc. of water was added to the above alcoholic solution and cooled in water. Then the resulting solution was left at room temperature overnight. After evaporation of the methanol under reduced pressure, the solution was extracted with chloroform. The chloroform extract was evaporated to dryness after being washed with water and then dried with anhydrous sodium sulfate. When ether was added to the resulting residue, 2 g. of the product was obtained. It crystallized readily from ethyl acetate in little buttons. After recrystallization from the same solvent, the compound melted at 152~154°C and did not depress the melting point of an authentic hydroxylycoctonine, prepared by silver oxide oxidation[7].

Hydroxylycoctonam (IX).— This compound was obtained by treatment analogous to that reported by Edwards and Marion[10]. To a solution of 5.32 g. of hydroxylycoctonine in 400 cc. of water was added 3.45 g. of powdered potassium permanganate in small portions at room temperature. After the addition of the entire amount of the oxidant, the reaction mixture was left at room temperature overnight, and the resulting manganese dioxide was filtered off. The filtrate was extracted with chloroform, and the resulting extract was washed with diluted hydrochloric acid and then with water. When the washed chloroform solution was evaporated, a resinous material remained. This material was crystallized by the addition of acetone-ether. It was recrystallized from acetone as a monohydrate, m. p. 200~203°C.

Anal. Found: C, 58.31; H, 7.98. Calcd. for $C_{25}H_{39}O_9N \cdot H_2O$: C, 58.24; H, 8.01%.

Oxidation of Hydroxylycoctonam (IX) with Chromic Anhydride.—In 10 cc. of 5% sulfuric acid solution, 0.51 g. of hydroxylycoctonam was treated with 0.4 g. of chromic anhydride in just the same way as described under oxidation of lycoctonam. The oxidation of this compound was slower than that of lycoctonam, and required more than a week. After reducing the oxidant

10) O. E. Edwards and Léo Marion: *Can. J. Chem.* **32**, 1146 (1954).

the solution was extracted with chloroform, and the extract was shaken with dilute aqueous ammonia. When the chloroform layer was evaporated, there remained resinous products a. Yield, 0.20 g. (see below).

The aqueous layer was acidified with dilute hydrochloric acid and then extracted with chloroform. On evaporation of the solvent, the chloroform extract gave acidic products which were crystallized by the addition of ether. These products were separated into two acids, one readily soluble in acetone and the other less soluble. The readily soluble acid was recrystallized from acetone-ethanol in prisms melting at 220~222°C (decomp.) after softening at 200°C. This acid was named C_1-acid. The less soluble acid was crystallized from hot water in plates, melting at 193~195°C. This acid was named Y-acid.

The neutral product a was separated into two parts, one insoluble in benzene and the other soluble. The insoluble part crystallized from acetone in small buttons, which weighed 80 mg. each and melted at 177~180°C after recrystallization from acetone. This neutral product was named Y. The benzene-soluble part, weighing 100 mg., was subjected to chromatography on alumina. Elution with 5% methanol in benzene gave a product which crystallized from acetone in rhombic forms, m. p. 226~227°C. This product was named Z.

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The Aconite Alkaloids. XXX. On Lucidusculine*

By Harusada SUGINOME, Takashi AMIYA and Takeo SHIMA

(Received November 15, 1958)

Lucidusculine, $C_{24}H_{35}O_4N$, was previously isolated from the roots of *Aconitum lucidusculum* Nakai by R. Majima and S. Morio[1,2], and studied by H. Suginome and his collaborators[3-5]. Lucidusculine is a monoacetate of a trihydric amino alcohol, luciculine, $C_{22}H_{33}O_3N \cdot H_2O$[2,5], which was obtained by hydrolysis of the former. The presence of an *N*-ethyl group was confirmed by the formation of mesoluciculine, $C_{21}H_{31}O_3N \cdot H_2O$[5], on Hofmann degradation of luciculine. Further, as lucidusculine absorbed one mole of hydrogen on catalytic hydrogenation, it was assumed that the base has one double bond[4].

On the basis of the above results, the partial structure of lucidusculine was previously represented as:

$$C_{20}H_{25}\begin{cases}(OH)_2\\OCOCH_3\\>N\text{-}C_2H_5\\1\,F\end{cases}$$

Luciculine shows absorption peaks in the infrared spectrum at 6.09 and 11.27 μ and lucidusculine diacetate[4] shows peaks at 6.08 and 11.32 μ. Nevertheless, dihydrolucidusculine diacetate shows no peak near the above-mentioned region[6]. These data suggest the presence of a terminal methylene group in each of luciculine and lucidusculine diacetate, which is also supported by the isolation of formaldehyde as the dimedone complex in ozonolysis experiment with lucidusculine and lucidusculine diacetate. Further, mesoluciculine gave 0.45 mol. of acetic acid on Kuhn-Roth oxidation, while dihydromesoluciculine[7] yielded 0.92 mol. of acetic acid on the same oxidation. The difference (0.47 mol.) can be explained by the following scheme:

$$\underset{\text{Mesoluciculine}}{>C=CH_2} \xrightarrow{H_2} \underset{\text{Dihydromesoluciculine}}{>CH-CH_3}$$

From these results and the biogenesis of the aconite alkaloids[8], the formula of

* The report, "Aconite Alkaloids. On Pyrolytic Products of Aconitine, Oxonitine, and their Derivatives", printed in This Bulletin, **31**, 658 (1958), constitutes Part XXXI. Part XXIX: H. Suginome, S. Imato, S. Yamada and N. Katsui, This Bulletin, **23**, 819 (1959).

1) R. Majima and S. Morio, *Proc. Imp. Acad. Tokyo*, **7**, 351 (1931).
2) R. Majima and S. Morio, *Ber.*, **65**, 559 (1932).
3) H. Suginome and F. Shimanouchi, *Ann.*, **545**, 222 (1940).
4) H. Suginome, S. Kakimoto and J. Sonoda, *J. Fac. Sci., Hokkaido Univ., Ser. III. Chem.*, **4**, 25 (1950).
5) H. Suginome and S. Umezawa, ibid., 44.
6) T. Amiya, unpublished work.
7) H. Suginome and S. Umezawa, *J. Fac. Sci., Hokkaido Univ., Ser., III. Chem.*, **4**, Supplement, 74 (1952).
8) R. H. F. Manske, H. L. Holmes, "The Alkaloids", Vol. IV, Academic Press, Inc., New York (1954), p. 280.

lucidusculine may be extended further as follows:

$$C_{19}H_{23}\begin{cases}(OH)_2\\OCOCH_3\\>N-C_2H_5\\>C=CH_2\end{cases}$$

Lucidusculine is assumed to have a hexacyclic structure based on the skeletal formula $C_{19}H_{29}N$[3].

Amiya and Nagaoka previously isolated lucidusculine and jesaconitine from the roots of *Aconitum* species from Shoya, Hidaka in Hokkaido[9]. Extraction with ethanol and the following treatment were done in the same way as in the case of other aconite roots[10], and these two alkaloids were isolated from the water-insoluble portion. Now, quantitative separation of these alkaloids from mother-roots and from daughter-roots of the above-mentioned *Aconitum* plants by Ochiai's chromatographic method[11] was tried. As a model experiment, aconitine, jesaconitine and lucidusculine were dissolved in chloroform which was saturated with concentrated ammonia water[12], the solution was passed through a column of alumina, and the column was eluted with chloroform-ammonia water, followed by acetone and then methanol. The residue from the chloroform-ammonia water elute was found to be composed of aconitine and jesaconitine and that from the acetone elute was composed of lucidusculine only. Thus, the same procedure was applied to the above-mentioned water-insoluble portions with results as follows:

Weights of dried roots	Water-insoluble portions	Crystalline alkaloids	
Mother-roots	4.4 g.	Jesaconitine	0.4 g.
4.5 kg.		Lucidusculine	0.2 g.
Daughter-roots	20.5 g.	Jesaconitine	1.4 g.
4.5 kg.		Lucidusculine	0.8 g.

Experimental

Ozonolysis of Lucidusculine.—Lucidusculine (95 mg.) was ozonized in 20 ml. of chloroform-acetic acid (1 : 1 by volume) at −25～−35°C with three moles of ozone. The solution was hydrogenated with 5% palladium-carbon for 15 min. After removal of the palladium-carbon, dimedone (75 mg.) was added to the solution. After standing overnight, the solvents were completely evaporated in vacuo. To the residue, 10% sodium hydroxide solution (5 ml.) was added. When the solution was washed with chloroform and acidified with hydrochloric acid, the crystalline dimedone-formaldehyde complex was separated. It was extracted with chloroform and the chloroform solution was evaporated in vacuo to give a crystalline residue. Recrystallization from ethanol yielded 10 mg. of the dimedone-formaldehyde complex, which melted at 190°C and showed no depression of the melting point on admixture with an authentic specimen.

Ozonolysis of Lucidusculine Diacetate.—Lucidusculine diacetate (350 mg.) was ozonized and treated in the same way. Thus, 65 mg. of the dimedone-formaldehyde complex was obtained.

Kuhn-Roth Oxidation.—Mesoluciculine and dihydromesoluciculine were oxidized by L. G. Ginger's method[13]. The results were as follows:

Mesoluciculine: *Anal.* Found: (C)-CH_3, 1.84 (0.45 mol.). Calcd. for $C_{21}H_{31}O_3N\cdot H_2O$: 1 (C)-$CH_3$, 4.13%.

Dihydromesoluciculine: *Anal.* Found: (C)-CH_3, 3.71 (0.92 mol.). Calcd. for $C_{21}H_{33}O_3N\cdot 1.5H_2O$: 1 (C)-$CH_3$, 4.01%.

Model Experiment of Separation.—Lucidusculine, aconitine and jesaconitine (100 mg. each) were dissolved in 10 ml. of chloroform-ammonia water, the solution was passed through a column (1.4 cm. in diameter) of 90 g. of alumina, and the column was eluted with 280 ml. of chloroform-ammonia water, 100 ml. of acetone and 100 ml. of methanol in succession. The chloroform-ammonia water elute gave 200 mg. of a residue. The solution of the residue (0.661 mg.) in methanol (10 ml.) gave an ultraviolet absorption spectrum, λ 220 mμ (E 0.69)[14], λ_{max} 232 mμ (E 0.91), λ_{min} 245 mμ (E 0.78) and λ_{max} 259 mμ (E 1.10). The solution of 0.323 mg. of aconitine and 0.323 mg. of jesaconitine in 10 ml. of methanol showed an identical ultraviolet spectrum[15]. The acetone elute gave 100 mg. of lucidusculine melting at 170°C alone and on admixture with an authentic specimen.

Isolation of Alkaloids.—The dried roots were divided into mother-roots and daughter-roots.

Isolation of alkaloids from mother-roots.—The mother-roots (4.5 kg.) were ground and percolated with ethanol. The percolate was treated as in the case of other aconite roots[10]. The water-insoluble portion (4.4 g.) was dissolved in 10 ml. of chloroform-ammonia water and the solution was passed through a column (1.4 cm. in diameter) of 90 g. of alumina, and the column was

9) T. Amiya and I. Nagaoka, Read before the 5th Annual Meeting of the Chemical Society of Japan, held in Tokyo, April, 1952, and the 6th Annual Meeting of the Chemical Society of Japan, held in Kyoto, April, 1953. The plants were collected by I. Nagaoka and the late T. Ichihashi in Sepetember, 1944.

10) H. Suginome, S. Furusawa, Y. Chiba and S. Kakimoto, *J. Fac. Sci., Hokkaido Univ., Ser. III. Chem.*, **4**, 1 (1950).

11) E. Ochiai, T. Okamoto, T. Sugasawa, H. Tani and S. Hung, *J. Pharm. Soc. Japan* (*Yakugaku Zasshi*), **72**, 816 (1952).

12) This solvent is designated as "chloroform-ammonia water".

13) L. G. Ginger, *J. Biol. Chem.*, **156**, 453 (1944).

14) $E=\log_{10} I_0/I$.

15) A. E. Gillam, E. S. Stern, "An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry", Edward Arnold Publishers, Ltd., London, (1954), p. 185; E. Ochiai, T. Okamoto and S. Sakai, *J. Pharm. Soc. Japan* (*Yakugaku Zasshi*), **75**, 545 (1955).

eluted with 280 ml. of chloroform-ammonia water, next with 100 ml. of acetone and then with 70ml. of methanol. The basic substance was obtained from the entire amount of the chloroform-ammonia water elute. It was purified as perchlorate by recrystallization from ethanol and 0.5 g. of pure perchlorate was obtained, m. p. 220~230°C (decomp.). The base (0.670 mg.) liberated from the perchlorate by means of ammonia water was dissolved in 10 ml. of methanol. The solution showed ultraviolet absorption, λ 220 mμ (E 0.55), λ_{min} 225 mμ (E 0.44) and λ_{max} 259 mμ (E 1.44). The solution of 0.130 mg. of aconitine and 0.540 mg. of jesaconitine in 10 ml. of methanol showed an identical ultraviolet spectrum. The spectral observations and the experiments mentioned below indicate that jesaconitine is contained in the material in an amount of about 80%[15,16].

The remaining portion of the free base was extracted with ether in a Soxhlet extractor for 3 hr.; and the extracted base was transformed into the perchlorate. The salt yielded 0.1 g. of the salt of "jesaconitine-rich base" upon recrystallization from ethanol. The purified salt had m. p. 230°C (decomp.), $[\alpha]_D^{25}$ −12.6° (methanol). The jesaconitine-rich base (0.673 mg.) prepared from the above salt was dissolved in 10 ml. of methanol. The solution showed ultraviolet absorption, λ 220 mμ (E 0.50), λ_{min} 225 mμ (E 0.32) and λ_{max} 259 mμ (E 1.79). The solution of 0.060 mg. of aconitine and 0.615 mg. of jesaconitine in 10 ml. of methanol showed an identical ultraviolet spectrum. The salt of the jesaconitine-rich base was analyzed.

Anal. Found: C, 53.72; H, 6.44; N, 2.06. Calcd. for $C_{35}H_{49}O_{12}N \cdot HClO_4$[17]: C, 54.15; H, 6.49; N, 1.80%.

After evaporation of the acetone elute in vacuo, the residue yielded 0.2 g. of lucidusculine by recrystallization from ethanol, m. p. 170°C with no depression on admixture with an authentic specimen.

Isolation of alkaloids from daughter-roots. — The water-insoluble portion (20.5 g.) from 4.5 kg. of the daughter-roots was treated in the same way as in the case of the mother-roots. The basic substance was obtained from the entire portion of the chloroform-ammonia water elute. The perchlorate of the base was recrystallized from ethanol. The free base liberated from the perchlorate was neutralized with 0.77 N hydrobromic acid. The solution of the resulting hydrobromide gave 0.08 g. of a crystalline material on standing[18]. The free base (0.665 mg.) prepared from the hydrobromide was dissolved in 10 ml. of methanol. The solution showed ultraviolet absorption, λ_{max} 232 mμ (E 0.90), λ_{min} 245 mμ (E 0.71) and λ_{max} 259 mμ (E 1.03). The solution of 0.356 mg. of aconitine and 0.309 mg. of jesaconitine in 10 ml. of methanol gave an identical ultraviolet spectrum.

The mother liquor from the hydrobromide was treated with ammonia water, yielding 1.7 g. of the free base. The solution of the free base (0.667 mg.) in 10 ml. of methanol showed ultraviolet absorption, λ 220 mμ (E 0.55), λ_{min} 225 mμ (E 0.44) and λ_{max} 259 mμ (E 1.53). The solution of 0.120 mg. of aconitine and 0.545 mg. of jesaconitine in 10 ml. of methanol showed an identical ultraviolet spectrum.

The spectral observations and the experiments described below indicate that jesaconitine was contained in an amount of about 80%.

The remaining portion of the above free base was extracted with ether in a Soxhlet extractor for 3 hr.; and the extracted base was transformed into the perchlorate. The crude perchlorate yielded 0.2 g. of the perchlorate of a jesaconitine-rich base upon recrystallization from ethanol. The purified perchlorate had m. p. 230°C (decomp.), $[\alpha]_D^{25}$ −14.8°C (methanol). The solution of jesaconitine-rich base (0.673 mg.), prepared from a part of the perchlorate, in 10 ml. of methanol showed ultraviolet absorption, λ 220 mμ (E 0.50), λ_{min} 225 mμ (E 0.32) and λ_{max} 259 mμ (E 1.79). The solution of 0.060 mg. of aconitine and 0.615 mg. of jesaconitine showed an identical ultaviolet spectrum. The purified perchlorate was analyzed.

Anal. Found: C, 53.92; H, 6.50; N, 1.91. Calcd. for $C_{35}H_{49}O_{12}N \cdot HClO_4$: C, 54.15; H, 6.49; N, 1.80%.

Hydrolysis of the ether-insoluble portion (1.1 g.) of the above base gave 50 mg. of anisic acid and 300 mg. of aconine hydrochloride, which melted at 176°C and was analyzed.

Anal. Found. C, 52.65; H, 8.16; N, 2.43. Calcd. for $C_{25}H_{41}O_9N \cdot HCl \cdot 2H_2O$: C, 52.48; H, 8.04; N, 2.45%.

The acetone elute gave 0.8 g. of lucidusculine as in the case of the mother-roots, m. p. 170°C with no depression on admixture with an authentic specimen.

Summary

1. In lucidusculine the presence of a double bond had previously been assumed. Further, on the basis of observations of the infrared spectra of luciculine, lucidusculine diacetate and dihydrolucidusculine diacetate, the presence of a terminal methylene group in lucidusculine was suggested.

Kuhn-Roth oxidation of mesoluciculine and of dihydromesoluciculine and ozonolysis of lucidusculine and of lucidusculine diacetate supported the suggested presence of a terminal methylene group. These results and the biogenesis of the aconite

16) On account of the the existence of the benzoyl ester of an alkaloidal amino alcohol, aconitine was assumed to be present.

17) If the salt is composed of 1 mol. of jesaconitine and 1/10 mol. of aconitine, the calculated values are: C, 54.19; H, 6.44%.

18) The benzoyl ester of an alkaloidal amino alcohol may be aconitine; this seems to be supported by the fact that the crystalline hydrobromide of the ester alkaloid is slighthly soluble in water.

alkaloids show that the double bond in lucidusculine belongs to a terminal methylene group.

2. The roots of *Aconitum* species from Shoya, Hidaka in Hokkaido, were divided into mother-roots and daughter-roots; the water-insoluble basic portions were obtained from both; lucidusculine and jesaconitine were isolated by the chromatographic method.

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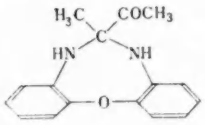
On the Structure of Condensation Products of o-Aminophenols with α-Dicarbonyl Compounds. I

By Ichiro MURASE

(Received December 11, 1958)

The condensation reaction between *o*-aminophenol and diacetyl was first carried out by Kehrmann in 1895, who tentatively suggested for the condensation product the eight-membered ring structure containing a diphenyl ether bond as shown in the formula A[1].



(A)

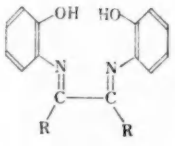
Recently, Bayer assigned Schiff base structures to the compounds obtained by the condensation of *o*-aminophenol with glyoxal and diacetyl and reported that glyoxal bis-(2-hydroxy anil) gave chelates with copper, nickel, cobalt, etc., but diacetyl bis-(2-hydroxy anil) did not form a metal chelate[2].

The present investigation was undertaken in order to confirm the structure of these condensation products.

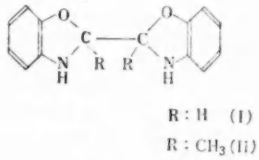
o-Aminophenol smoothly condensed with glyoxal and with diacetyl by heating the mixture in an aqueous or alcoholic solution. The product I from glyoxal was colorless needles, m. p. 210°C*, and the product II from diacetyl was colorless plates, m. p. 241°C**.

The Schiff base structure is represented as the formula B.

It was confirmed in some cases that condensation products of *β*-aminoalcohols and carbonyl compounds are oxazolidine or equilibrium mixtures of the Schiff base with the former[3]. Along with these facts, the alternative structure of I and II is bibenzoxazoline (C).



(B)



R : H (I)
R : CH_3 (II)

(C)

Only a few instances of benzoxazoline structure were reported concerning the condensation products of *o*-aminophenols and carbonyl compounds[4], but their structures were not always confirmed exactly. It has been accepted that the benzoxazole owes its formation to pyrolysis of the benzoxazoline primarily formed in the condensation of *o*-aminophenol with ketone[5].

1) F. Kehrmann, *Ber.*, **28**, 343 (1895).
2) E. Bayer, *Ber.*, **90**, 2325 (1957).
* According to Bayer, the melting point of the product I is 204°C.
** The melting point of II is 227°C according to Bayer, but Kehrmann reported it as being 239~240°C.

3) G. E. McCasland and C. Horswill, *J. Am. Chem. Soc.*, **73**, 3923 (1951); H. R. Nace and M. H. Gollis, ibid., **74**, 5189 (1952); J. Metzger and A. Pacault, *Rec. trav. chim.*, **71**, 259 (1952); E. P. Goldberg and H. R. Nace, *J. Am. Chem. Soc.*, **75**, 6260 (1953); E. D. Bergmann, E. Gil-Av and S. Pinchas, *Rec. trav. chim.*, **71**, 168 (1952); *J. Am. Chem. Soc.*, **75**, 358 (1953); H. R. Nace and E. P. Goldberg, ibid., **75**, 3646 (1953).
4) A. Hantzsch, *Ber.*, **16**, 1948 (1883); Schroeter et al., *Ann.*, **426**, 83 (1922); F. Sachs and W. Brunetti, *Ber.*, **40**, 3234 (1907); L. Calatis, ibid., **66**, 1774 (1933).
5) Elderfield, "Heterocyclic Compound", Vol. 5, John Wiley & Sons, Inc., New York, (1957), p. 431.

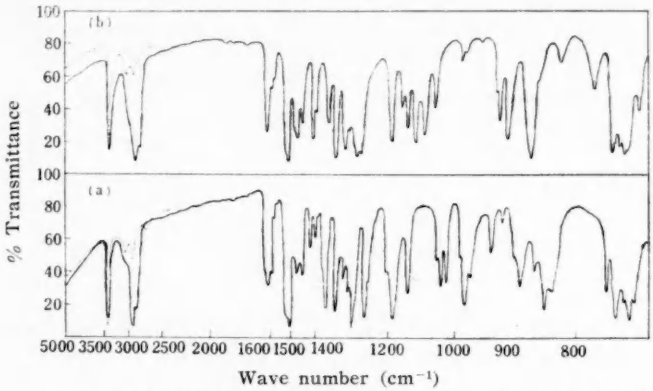


Fig. 1. Infrared spectra of the compounds. I : a and II : b, —— Nujol mull, ····· hexachlorobutadiene mull.

TABLE I. INFRARED ABSORPTION SPECTRA OF I, II AND RELATED SCHIFF BASES NEAR 3000 cm^{-1} AND 1600 cm^{-1} REGION

I	II	Diacetyl dianil	Glyoxal bis-(4-hydroxy anil)	Glyoxal bis-(4-dimethyl-amino anil)	Salicyl-idene *o*-amino-phenol	Bissalicyl-aldehyde ethylene-diimine	Assignment
3378	3358						NH stretching
		1631	1610	1605	1631	1631	Conjugated C=N
1613	1613						
1600	1587	1587	1595		1619	1613	
1585	1580	1577	1580	1567	1597	1582	Phenyl ring
1499	1497	1490	1513	1517	1531	1506	

Eventually, a Schiff base structure or an oxazoline structure will be the only choice offered for the determination of the structure of the condensation products of *o*-aminophenol with glyoxal and diacetyl. The following investigations led to the conclusion that the structures of these are not so much a Schiff base type as an oxazoline type.

Behaviors to Mineral Acid and Aqueous Alkali.—I and II are insoluble in dilute mineral acids and stable to such an extent that they are not hydrolyzed after standing overnight at room temperature with 3 N hydrochloric acid, but hydrolyzed by heating with 6 N hydrochloric acid; thus they were gradually hydrolyzed and *o*-aminophenol hydrochloride was obtained quantitatively. I and II were not only insoluble in dilute aqueous alkali, but also stable at room temperature. On heating them with a ten per cent aqueous sodium hydroxide solution, *o*-aminophenol was obtained and identified as the *N*-acetyl derivative.

Spectroscopic Investigation. — Infrared and ultraviolet absorption spectra of I and II are shown In Figs. 1 and 2 respectively***. The assignment of the infrared absorption bands and the ultraviolet absorption maxima are summarized and compared with those of the related Schiff bases in Tables I and II, respectively.

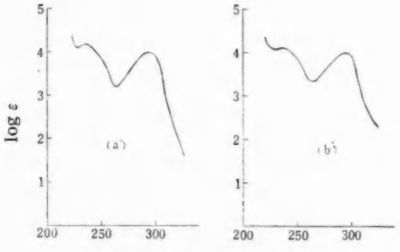


Fig. 2. Absorption curve of the compounds I (a') and II (b'), (ethanol solution).

*** The infrared spectra were obtained with a Perkin-Elmer Model 21 and an Oyōkōken D-201 spectrometer using NaCl prism. Ultraviolet spectra were obtained with a Beckman Model DK-2 spectrometer.

TABLE II. THE ULTRAVIOLET ABSORPTION SPECTRA OF I, II AND RELATED SCHIFF BASES IN ETHANOL

Compound	λ (mμ)	ε	λ (mμ)	ε	λ (mμ)	ε
I	236	14340	294	9880		
II	236	13200	293	9880		
Diacetyl dianil	227	40700			332	4360
Glyoxal bis-(4-hydroxy anil)	244	13200	296	8300	383	23980
Glyoxal bis-(4-dimethyl-amino anil)	253	15760	318	5700	450	37200

If the Schiff base structure (B) is adopted, the bands in the 3000 cm^{-1} region of infrared are assigned to OH vibration, 1613 cm^{-1} being a C=N vibration shifted by the strong conjugation in the same manner as in the case of the Schiff bases quoted.

Intermolecular hydrogen bondings, however, should be present in this case; a hydrogen bonding causes a shift of the OH stretching band to the lower frequency and broadening of the band[6]. From these circumstances, the shape and the position of these bands (Fig. 1) are more plausibly explained to correspond to the NH vibration. Furthermore, the ultraviolet absorption spectra of I and II (Fig. 2) are closely related to that of *o*-aminophenol itself (λ_{max} 232 mμ, ε_{max} 7240; λ_{max} 286 mμ, ε_{max} 4270)[7], thus the presence of the chromophore, such as conjugated azomethine linkages which cause a bathochromic effect, should be discounted.

It is well known that a compound having an anilino structure has an infrared absorption band near 1600 cm^{-1} region[8]. From the investigations of indolenine derivatives, Witkop and Patrick[9] have quoted a band at 1613 cm^{-1} as being typical of the structure C_6H_5–NH–$\overset{|}{\underset{|}{C}}$–. Since the structure of bibenzoxazoline (C) resembles that of indolenine and an absorption similar to that of the latter is present at 1613 cm^{-1}, the author concluded the absorption to be caused by the same structural element, and at least shouldered bands are regarded as phenyl ring vibrations; it is not completely clear whether this absorption arises from an NH deformation or from a phenyl ring.

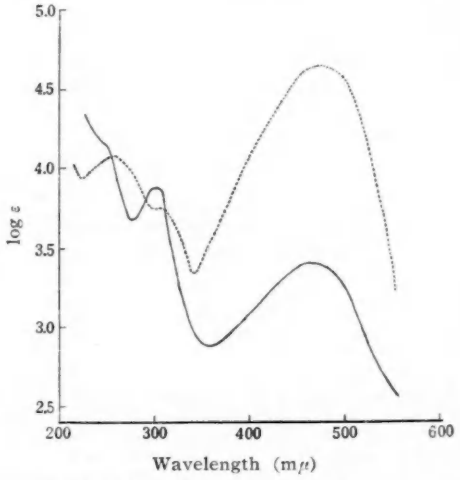


Fig. 3. Absorption curve of the compound I+KOH: —— and glyoxal bis-(4-hydroxy anil)+KOH: ·····.

Although compound I was insoluble in aqueous alkali, a reddish yellow color was produced when an excess of potassium hydroxide was added to its ethanol solution, and another absorption maximum was observed at 467 mμ (ε, 2445) as shown in Fig. 3.

In the case of glyoxal bis-(4-hydroxy anil), the absorption maximum shifted from 367 mμ to 470 mμ when potassium hydroxide was added. The explanation of this phenomenon is that when a proton acceptor such as a hydroxyl ion is present in the ethanol solution, bibenzoxazoline (C′) tautomerizes to Schiff base B′ under ring opening. The above consideration is tenable in view of the fact that oxazolidine tautomerizes to Schiff base resulting in an equilibrium mixture of the two structures[3].

The curve in Fig. 4 means that the Schiff base is produced as a result of tautomerism and the solution reaches an equilibrium. The curve comes up again after standing for a long time, because hydrolysis sets in.

The formation of a metal chelate I is also explained by the tautomeric change.

6) L. J. Bellamy, "The Infrared Spectra of Complex Molecules", John Wiley & Sons, Inc., New York, (1954), p. 86.
7) R. A. Friedel, M. Orchin, "Ultraviolet Spectra of Aromatic Compounds", John Wiley & Sons, Inc., New York, (1951).
8) Reference 6, p. 219.
9) B. Witrop and J. B. Patrick, *J. Am. Chem. Soc.*, 73, 713 (1951).

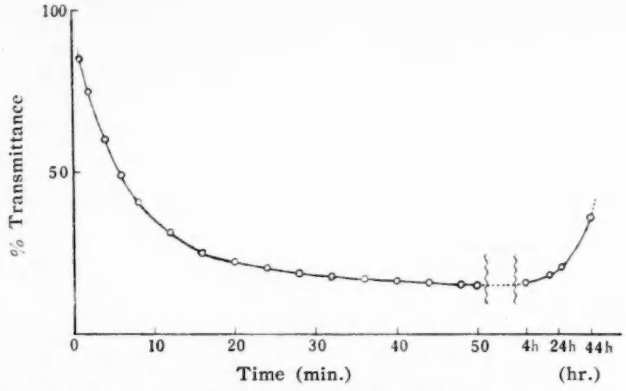


Fig. 4. Variation of the transmittance of the absorption maximum of I in ethanol (about 1/2000 mol.) at 470 mμ after the addition of potassium hydroxide.

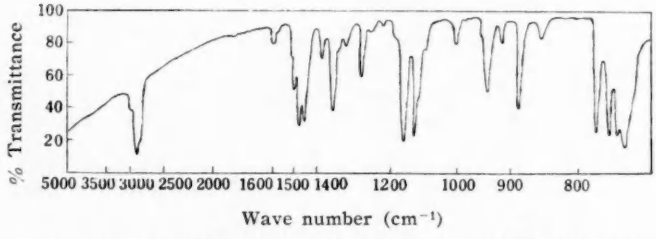


Fig. 5. Infrared spectrum of 2,2'-bibenzoxazole (Nujol mull).

When metal acetate has been added to the solution, an acetate ion acts as a proton acceptor and an anion of Schiff base is produced in the same manner as in the case of potassium hydroxide. The structure of a metal chelate thus formed, has been represented by Bayer as an ionic one of glyoxal bis-(2-hydroxy anil).

Compound II failed to give a new absorption band at a visible region on addition of potassium hydroxide to its ethanol solution. Accordingly, II lacks the feature of tautomerism in contrast with I, and the inability to form a metal chelate is well understood.

Chemical Properties.—Methylation of I and II was attempted using sodium amide and methyl iodide in dioxane or diazomethane in ether, but only an unchanged material was recovered.

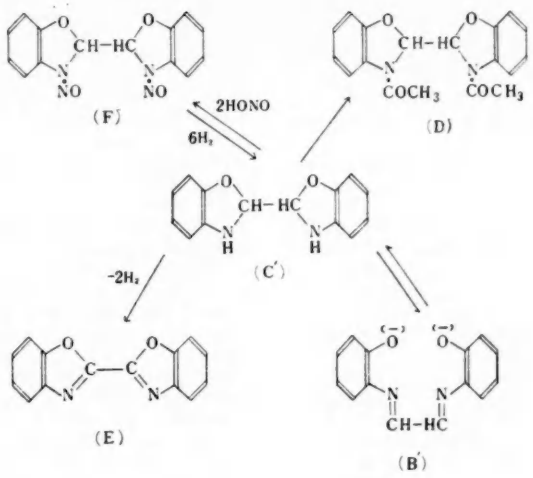
By the acetylation of I with acetic anhydride, a crystalline diacetyl derivative was obtained, m. p. 263~265°C. It was not hydrolyzed by acid or alkali and the infrared spectrum showed absorptions at 1670 cm^{-1} (C=O stretching) and 1587 cm^{-1} (phenyl ring) and no absorption was observed in the 3000 cm^{-1} region. Thus, the diacetyl derivative proved to be *N,N'*-diacetyl-2,2'-bibenzoxazoline(D).

When the dilute solution of I in acetone was carefully treated with potassium permanganate, a dehydrogenation product was obtained in pale yellow prisms, m. p. 257°C. It was confirmed to be 2,2'-bibenzoxazole (E) from mixed melting point test with the authentic sample[10] prepared by the oxidative condensation of benzoxazole with copper acetate. 2,2'-Bibenzoxazole was also obtained by the oxidation of I with lead dioxide in benzene. The infrared absorption pattern (Fig. 5) of the dehydrogenation product was quite identical with that of the authentic sample.

Similar oxidation did not proceed in the case of II under the same conditions.

By the nitrosation of I, yellow dinitroso derivative (F) was obtained. It has no absorption band near 3000 cm^{-1} of infrared; the substitution of nitroso group occurred at imino hydrogen in the bibenzoxazoline (C'). By the catalytic hydrogenation of

10) D. R. Pat., 650,050 (1936); *Chem. Zentr.*, **1937**, II, 4395.



F, six moles of hydrogen were absorbed and I was reproduced.

The above reactions are summarized in the following schema.

Thus, the most reasonable conclusion to be drawn from the available data is that the condensation product of *o*-aminophenol with glyoxal is 2,2′-bibenzoxazoline and with diacetyl is 2,2′-dimethyl-2,2′-bibenzoxazoline as shown in the formula C. Bayer's investigation concerning the structure of metal chelates would be supported along with the consideration that 2,2′-bibenzoxazoline tautomerizes to glyoxal bis-(2-hydroxy anil).

Condensation products of many other *α*-dicarbonyl compounds with *o*-aminophenol derivatives and their structures will be reported in the subsequent paper.

Experimeatal

2, 2′-Dimethyl-2, 2′-bibenzoxazoline. — Prepared from *o*-aminophenol and diacetyl according to Kehrmann's method. Colorless plates, m. p. 241°C. The substance afforded a deep reddish violet color when dissolved in concentrated sulfuric acid. The aqueous alcoholic solution did not show the color reaction with ferric chloride.

Anal. Found: C, 71.97; H, 6.22; N, 10.52. Calcd. for $C_{16}H_{16}N_2O_2$: C, 71.67; H, 6.01; N, 10.44%.

2, 2′-Bibenzoxazoline.—To a solution of 10 g. of *o*-aminophenol in 90 ml. of hot ethanol, 15 g. of 30% aqueous glyoxal was added and gently refluxed for thirty minutes. The mixture became dark brown and the crystals separated out. The crystals collected after being cooled were washed with ethanol to give almost colorless ones. Recrystallization from ethanol using a Norit gave colorless needles, m. p. 210°C. Yield, 6 g.

2,2′-Bibenzoxazoline is soluble in methanol, benzene and dioxane and insoluble in water and chloroform. The substance afforded a deep green color when dissolved in concentrated sulfuric acid.

Anal. Found: C, 70.34; H, 4.86; N, 11.30. Calcd. for $C_{14}H_{12}N_2O_2$: C, 69.99; H, 5.03; N, 11.66%.

Acetylation of 2, 2′-Bibenzoxazoline : *N*, *N*′-Diacetyl-2-2′-bibenzoxazoline. — A solution of 0.5 g. of 2,2′-bibenzoxazoline in 20 ml. of acetic anhydride was gently refluxed for ca. 2 hr. The reaction mixture became dark brown. The solvent was removed under reduced pressure, and the resulting dark brown tarrish residue was treated with a small amount of benzene, filtered, and the remaining crystals were washed with benzene and methanol, and recrystallized from dilute acetic acid. Colorless crystals, m. p. 263～265°C, were obtained in a poor yield.

This diacetyl derivative is slightly soluble in benzene and soluble in dioxane and afforded a red color in warm concentrated sulfuric acid.

Anal. Found: C, 66.17; H, 4.97; N, 8.67. Calcd. for $C_{18}H_{16}N_2O_4$: C, 66.65; H, 4.97; N, 8.67%.

Potassium Permanganate Oxidation of 2, 2′-Bibenzoxazoline : 2, 2′-Bibenzoxazole.—To a solution of 0.5 g. of 2,2′-bibenzoxazoline in a mixture of 250 ml. of pure acetone and 50 ml. of water, 0.5 g. of potassium permanganate in 100 ml. of acetone was added dropwise with stirring and gentle boiling. The addition required ca. 3 hr. and the reaction mixture was boiled for an additional 1 hr. After being kept overnight, the reaction mixture was filtered and the filtrate was concentrated under reduced pressure. The yellowish brown residue was recrystallized twice from dioxane and then from chlorobenzene to give pale yellow prisms, m. p. 257°C.

Anal. Found: C, 71.27; H, 3.52; N, 11.60. Calcd. for $C_{14}H_8N_2O_2$: C, 71.18; H, 3.41; N, 11.86%.

Lead Dioxide Oxidation of 2, 2'-Bibenzoxazoline : 2, 2'-Bibenzoxazole. — To a solution of 2, 2'-bibenzoxazoline in 80 ml. of hot benzene, was added 20 g. of lead dioxide. The mixture was refluxed for ca. 6 hr. and turned dark brown. The hot mixture was filtered and the solvent was distilled off. The reddish brown residue was treated with alcohol, dried and dissolved in 20 ml. of benzene. The benzene solution was chromatographed over commercial activated alumina and developed with the same solvent. The first fraction which was obtained almost unabsorbed amounted to ca. 100 ml.; the solvent was removed by evaporation, the pale yellow residue was treated with hot alcohol and recrystallized twice from dioxane to give pale yellow crystals, m. p. 256°C. Mixed melting point with the authentic sample showed no depression.

Nitrosation of 2, 2'-Bibenzoxazoline. — A mixture of 1 g. of 2, 2'-bibenzoxazoline in 130 ml. of benzene and 1.1 g. of sodium nitrite in 20 ml. of water was warmed at 50°C and stirred vigorously. To the mixture, 10 ml. of 1 N hydrochloric acid was gradually added; then the benzene layer became yellow. The benzene layer which separated was washed with water and dried over anhydrous sodium sulfate. The solvent was distilled off under reduced pressure and the residue was recrystallized from ca. 150 ml. of alcohol to yield yellow needles, m. p. 157°C (decomp.).

This dinitroso derivative was not hydrolyzed even by boiling with dilute mineral acid or aqueous alkali, but dissolved in concentrated sulfuric acid with a green color and evolution of nitrogen monoxide (potassium iodide starch paper test).

Anal. Found: C, 56.36; H, 3.47; N, 18.13; mol. wt. (cryoscopic method, benzene), 301. Calcd. for $C_{14}H_{10}N_4O_4$: C, 56.39; H, 3.36; N, 18.77%; mol. wt., 298.27.

Hydrogenation of *N*, *N'*-Dinitroso-2, 2'-bibenzoxazoline. — A solution of 0.1 g. of the dinitroso compound in ca. 50 ml. of alcohol was hydrogenated using Adams catalyst at atmospheric pressure and room temperature. The yellow solution became colorless on absorption of a slight excess of hydrogen. The catalyst was filtered and the filtrate was evaporated under reduced pressure. The remaining crystals were recrystallized from alcohol, colorless plates, m. p. 209°C (decomp.). The substance was identical with 2, 2'-bibenzoxazoline. From the gas in the hydrogenation vessel, ammonia was detected (Nessler's reagent).

Glyoxal Bis-(4-hydroxy anil).—To a solution of 1 g. of freshly recrystallized *p*-aminophenol in a small amount of 80% alcohol, was added 1.2 g. of 30% aqueous glyoxal, and the mixture was heated on a water bath for several minutes. Then, crystals were separated out and the mixture was cooled and filtered. Recrystallization from a large amount of alcohol gave yellow needles, m. p. 212~213°C (decomp.).

Anal. Found: C, 70.04; H, 5.10; N, 11.47. Calcd. for $C_{14}H_{12}N_2O_2$: C, 69.99; H, 5.03; N, 11.66%.

The author wishes to express his thanks to Professor Tokuichi Tsumaki and Professor Takeichi Nishikawa for their exceedingly kind direction of this work. The author also thanks Dr. Yo Ueda and Mr. Hiroshige Yano of the Department of Pharmacy for their measurement of infrared and ultraviolet spectra and Mr. Michio Shido and Miss Sachiko Indo for microanalysis.

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Polarographic Studies of Metallic Complexes. V[1]. *Tetrammine Series of Cobalt(III) Complexes*[2]

By Nobufumi MAKI, Yoichi SHIMURA and Ryutaro TSUCHIDA

(Received December 24, 1958)

In the earlier papers of this series[1,3] the orders of the polarographic stability were determined for cobalt(III) complexes of pentammine and bisethylenediamine series, $[Co(NH_3)_5X]$, $[Co\ en_2X_2]$ or $[Co\ en_2Y]$. For the same purpose, the comparison of the half-wave potentials of the first waves has been carried out for the cobalt(III) complexes of tetrammine series, $[Co(NH_3)_4X_2]$ or $[Co(NH_3)_4Y]$, which has been briefly reported in the present paper. Some studies[4-10] were found in literature for the hexammine and the tetrammine cobalt(III) complexes of $[Co(NH_3)_4X_2]$ type, but few reports were found on the $[Co(NH_3)_4Y]$ type[10].

Experimental

A Yanagimoto model 104 polarograph similar to that previously described[1] was used to obtain the polarograms. The rate of flow of mercury, m, and the drop time, t, of the dropping mercury electrode were 0.635 mg./sec. and 6.92~7.32 sec., respectively, being measured in the solution of 0.1 F potassium chloride or 0.5 F potassium sulfate at an open circuit with a mercury head of 66.5 cm. A saturated calomel electrode (S.C.E.) was used for a reference electrode and connected to the cell solution through an agar bridge. The cell temperature was maintained at 25±0.1°C by means of a water thermostat. For accurate evaluation of curves and half-wave potentials the method previously described[10] was used. The oxygen dissolved in solution was expelled by passing a stream of nitrogen through the cell solution for an hour prior to each electrolysis. The reversibilities of the electrode reactions were examined by determining the slopes of $\log i/(i_d-i)$ vs. potential. The slopes of the log plots indicated irreversible reduction throughout.

The complex compounds studied were prepared by the methods described in literature. (The references are given in Tables I and II.) Each solution for electrolysis was made freshly from the dry crystalline cobalt(III) complexes before use and the polarographic measurements were made as soon as possible after the removal of oxygen. The concentration of the solution was 0.001 gram complex ion per litre. No maximum suppressor was used for the purpose of comparing the half-wave potentials of the complexes with one another. The presence of the maximum suppressor causes the lowering of the diffusion current and the shift of the half-wave potential to the negative direction. For instance, the half-wave potential of the first wave of the complex,

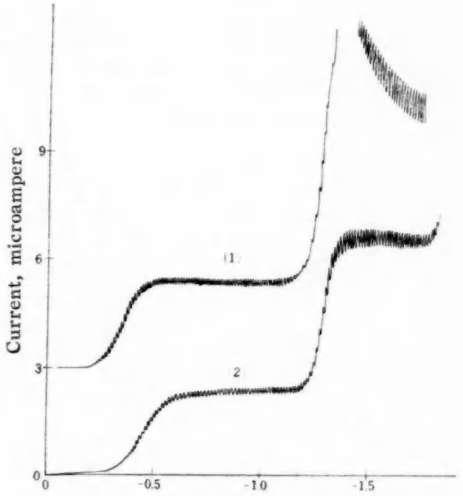


Fig. 1. The polarograms of alaninato-tetramminecobalt(III) complex, $[Co(NH_3)_4$ alan$]SO_4$, obtained in 0.5 F K_2SO_4 solution at the concentration of 0.001 F.
1. In the absence of the maximum suppressor.
   $E_{1/2}$ of 1st wave $=-0.32$ V.
2. In the presence of 0.0032% Tween-80.
   $E_{1/2}$ of 1st wave $=-0.44_5$ V.
   $E_{1/2}$ of 2nd wave $=-1.28_3$ V.

1) Part IV of this series; N. Maki, Y. Shimura and R. Tsuchida, This Bulletin, **32**, 150 (1959).
2) Partly presented at the Eleventh Annual Meeting of the Chemical Society of Japan, Tokyo, April 6, 1958.
3) N. Maki, Y. Shimura and R. Tsuchida, This Bulletin, **32**, 23 (1959).
4) J. B. Willis, J. A. Friend and D. P. Mellor, *J. Am. Chem. Soc.*, **67**, 1680 (1945).
5) H. F. Holtzclaw, Jr., ibid., **73**, 1821 (1951).
6) H. F. Holtzclaw, Jr. and D. P. Sheetz, ibid., **75**, 3053 (1953).
7) H. F. Holtzclaw, Jr. *J. Phys. Chem.*, **59**, 300 (1955).
8) H. A. Laitinen, J. C. Bailar, H. F. Holtzclaw, Jr. and J. V. Quagliano, *J. Am. Chem. Soc.*, **70**, 2999 (1948).
9) H. A. Laitinen, A. J. Frank and P. Kivalo, ibid., **75**, 2865 (1953).
10) N. Maki, Y. Shimura and R. Tsuchida, This Bulletin, **30**, 909 (1957).

TABLE I. HALF-WAVE POTENTIALS OF COBALT(III) COMPLEXES OF $[Co(NH_3)_4X_2]$ TYPE

Complex	Supporting electrolyte 0.5 F K_2SO_4			Supporting electrolyte 0.1 F KCl		
	$E_{1/2}$ of the 1st wave Co(III)→Co(II)	$E_{1/2}$ of the wave of aquated species Co(III)→Co(II)	$E_{1/2}$ of the 2nd wave Co(II)→Co(0)	$E_{1/2}$ of the 1st wave Co(III)→Co(II)	$E_{1/2}$ of the wave of aquated species Co(III)→Co(II)	$E_{1/2}$ of the 2nd wave Co(II)→Co(0)
$NH_4[Co(NH_3)_4(SO_3)_2]\cdot 3H_2O$[11]	−0.63		—**	−0.57		−1.25
cis-$[Co(NH_3)_4(OH_2)_2](SO_4)_3\cdot 3H_2O$[12]	-0.48_5		—**	-0.40_2		−1.25
$[Co(NH_3)_6](ClO_4)_3$[13]	-0.43_8		−1.28	-0.23_5		*prewave*
trans-$[Co(NH_3)_4(NO_2)_2]ClO_4$[14]	-0.20_7*		-1.28_1*	−0.21		
cis-$[Co(NH_3)_4(NO_2)_2]ClO_4$[14]	-0.04_3*		-1.28_3*	-0.04_8		
trans-$[Co(NH_3)_4Cl_2]Cl$[15]	+	−0.42	—**	+	−0.40	—**
cis-$[Co(NH_3)_4Cl_2]Cl$[16]	+	−0.42	—**	+	−0.40	—**
$[Co(NH_3)_4(IO_3)_2]IO_3\cdot HIO_3$[17]	+		*hydrogen wave*	+		*hydrogen wave*

The concentration of complex: 0.001 gram complex ion per litre. Potential unit: V. vs. S.C.E. Temp.: 25°C.

* The data quoted from J. B. Willis, J. A. Friend and D. P. Mellor, *J. Am. Chem. Soc.*, **67**, 1680 (1945).

** Maximum wave

TABLE II. HALF-WAVE POTENTIALS OF TETRAMMINE COBALT(III) COMPLEXES CONTAINING ONLY ONE CHELATE RING

Complex	Supporting electrolyte 0.5 F K_2SO_4		Supporting electrolyte 0.1 F KCl	
	$E_{1/2}$ of the 1st wave Co(III)→Co(II)	$E_{1/2}$ of the 2nd wave Co(II)→Co(0)	$E_{1/2}$ of the 1st wave Co(III)→Co(II)	$E_{1/2}$ of the 2nd wave Co(II)→Co(0)
$[Co(NH_3)_4en]_2(SO_4)_3\cdot 4H_2O$[18]	−0.44	—*	−0.27	—*
$[Co(NH_3)_4gly]SO_4\cdot H_2O$[19]	-0.40_5	—*	-0.23_4	—*
$[Co(NH_3)_4CO_3]_2SO_4\cdot 3H_2O$[20]	−0.37	−1.28	-0.30_5	−1.24
$[Co(NH_3)_4alan]SO_4$[19]	−0.32	—*	-0.20_5	—*
$[Co(NH_3)_4ox]Cl$[21]	-0.29_5	—*	−0.19	—*
$[Co(NH_3)_4leuc](ClO_4)_3$[22]	-0.25_5	—*	—*	—*
$[Co(NH_3)_6](ClO_4)_3$[13]	-0.43_8	*prewave*	-0.23_5	*prewave*

The concentration of complex: 0.001 gram complex ion per litre. Potential unit: V. vs. S.C.E. Temp.: 25°C.

* Maximum wave

$[Co(NH_3)_4alan^*]SO_4$, shifts towards the negative direction by -0.12_5V. (vs. S.C.E.) in the presence of 0.0032% Tween-80**, as is shown in Fig. 1.

The supporting electrolytes used are 0.1 F potassium chloride and 0.5 F potassium sulfate.

Results and Discussion

In Tables I and II are shown the half-wave potentials of the cobalt(III) complexes of tetrammine series.

All the compounds are reduced irreversibly in two steps at the dropping mercury electrode in 0.1 F potassium chloride or 0.5 F potassium sulfate except the complexes which aquate easily in solution. The ratio of the height of the first wave to that of the second is approximately 1:2. The heights of the first and the second waves are roughly proportional to the concentration of the complex ion at the concentration of $5\times10^{-3}\sim10^{-4}$ gram complex ion per litre. Consequently, it is considered that the first wave, corresponding to a gain of one electron, represents the reduction to cobalt(II) state and the second, corresponding to two electrons, represents the reduction to the metal. The half-wave potentials of the latter are always close to that of the hexaquocobalt(II) ion, $[Co(OH_2)_6]^{2+}$. ($E_{1/2}=-1.428$ V. vs. S.C.E. in 0.5 F K_2SO_4 solution[9].)

The reduction processes of tetrammine cobalt(III) complexes are considered as follows:

$$[Co(NH_3)_4X_2]^{(3-2n)+}+e^- \rightarrow [Co(NH_3)_4X_2]^{(2-2n)+}$$

$$[Co(NH_3)_4X_2]^{(2-2n)+}+mH_2O \xrightarrow[\text{rapidly}]{}$$

$$\begin{cases} [Co(OH_2)_6]^{2+}+2X^{n-}+4NH_3 \\ [Co(OH_2)_5X]^{(2-n)+}+X^{n-}+4NH_3 \\ [Co(OH_2)_4X_2]^{(2-2n)+}+4NH_3 \\ \text{etc.} \end{cases}$$

$$\begin{cases} [Co(OH_2)_6]^{2+}+2e^- \rightarrow Co+6H_2O \\ [Co(OH_2)_5X]^{(2-n)+}+2e^- \rightarrow Co+5H_2O+X^{n-} \\ [Co(OH_2)_4X_2]^{(2-2n)+}+2e^- \rightarrow Co+4H_2O+2X^{n-} \\ \text{etc.} \end{cases}$$

From the above scheme of the reduction it may be seen that the first step in the polarographic reduction of these cobalt(III) complexes corresponds to the disruption of the complexes, so its half-wave potential may be regarded as a measure of the stability against the polarographic reduction.

The polarographic stability of the cobalt(III) complexes of tetrammine series increases in the following order of the ligands; for the complexes of $[Co(NH_3)_4X_2]$ type,

$$IO_3^-,\ Cl^- < NO_2^- < NH_3 < OH_2 < SO_3^{2-}$$

(supporting electrolyte; 0.5 F K_2SO_4)

and for the complexes of $[Co(NH_3)_4Y]$ type,

$$leuc^- < ox^{2-} < alan^- < CO_3^{2-} < gly^- < en$$

(supporting electrolyte; 0.5 F K_2SO_4)

The order of the stability for the latter type was found to be altered between carbonate and ethylenediamine in the supporting electrolyte of 0.1 F potassium chloride.

$$leuc^- < ox^{2-} < alan^- < gly^- < en < CO_3^{2-}$$

(supporting electrolyte; 0.1 F KCl).

No special relation between the orders of the polarographic stability and that of the spectrochemical series could be found.

The half-wave potentials of the first waves for the complexes of the tetrammine series, $[Co(NH_3)_4X_2]$ or $[Co(NH_3)_4Y]$, exhibit always less negative values than those of the corresponding complexes of bisethylenediamine series, $[Co\ en_2X_2]$ or $[Co\ en_2Y]$, as is shown in Table III. This means that the two ethylenediamine chelate rings have the ability of forming the more stable cobalt(III) complexes against the polarographic reduction than the coordination of the corresponding four ammonia ligands. The result is quite in agreement with that obtained in the previous paper[10].

Fig. 2 shows the polarograms of *cis*-diaquotetramminecobalt(III) ion, $[Co(NH_3)_4(OH_2)_2]^{3+}$, in neutral supporting electrolyte. The slope of the tangent at the half-wave potential of the first wave is very small and the current rising gradually near the zero potential just like a residual current was observed as well as in the case of

* The following abbreviations are used; gly, $NH_2CH_2COO^-$; alan, $NH_2CH(CH_3)COO^-$; leuc, $(CH_3)_2CHCH_2CH(NH_2)COO^-$; ox, $(COO)_2^{2-}$; en, $NH_2CH_2CH_2NH_2$.

** Polyoxyethylene sorbitane monooleate.

11) A. Werner and H. Grüger, *Z. anorg. Chem.*, **16**, 398 (1898).
12) S. M. Jörgensen, ibid., **2**, 279 (1892).
13) M. Linhard, *Z. Elektrochem.*, **50**, 224 (1944).
14) S. M. Jörgensen, *Z. anorg. Chem.*, **17**, 455 (1898).
15) S. M. Jörgensen, ibid., **14**, 404 (1897).
16) C. Duval, *Compt. rend.*, **182**, 636 (1926).
17) N. I. Lobanov, *Obschei Neorg. Khim., Akad. Nauk S. S. S. R.*, **28**, 277 (1954). *Chem. Abstr.* **49**, 14555e.
18) Y. Shimura, This Bulletin, **31**, 311 (1958).
19) Y. Shimura, ibid., **31**, 173 (1958).
20) S. M. Jörgensen, *Z. anorg. Chem.*, **2**, 279 (1892).
21) S. M. Jörgensen, ibid., **11**, 416 (1896).
22) Y. Shimura, This Bulletin, **31**, 315 (1958).

TABLE III. COMPARISON OF THE HALF-WAVE POTENTIALS OF THE FIRST WAVES IN THE COBALT(III) COMPLEXES OF BISETHYLENEDIAMINE SERIES AND OF THE CORRESPONDING TETRAMMINE SERIES

Complex	Supporting electrolyte 0.5 F K_2SO_4 $E_{1/2}$ of the 1st wave Co(III)→Co(II)	Supporting electrolyte 0.1 F KCl $E_{1/2}$ of the 1st wave Co(III)→Co(II)
[Co en$_2$CO$_3$]Cl·H$_2$O	−0.45$_5$	−0.40
[Co(NH$_3$)$_4$CO$_3$]$_2$SO$_4$·3H$_2$O	−0.37	−0.30$_5$
[Co en$_2$ gly]Cl$_2$·H$_2$O	−0.41	−0.36
[Co(NH$_3$)$_4$gly]SO$_4$	−0.40$_5$	−0.23$_4$
[Co en$_2$ox]Cl	−0.31	−0.32
[Co(NH$_3$)$_4$ox]Cl	−0.29$_5$	−0.19
[Co en$_2$leuc](ClO$_4$)$_2$	−0.30$_5$	−0.33$_5$****
[Co(NH$_3$)$_4$leuc](ClO$_4$)$_2$	−0.25$_5$	——*
cis-[Co en$_2$(OH$_2$)$_2$](NO$_3$)$_3$	−0.50	−0.42
cis-[Co(NH$_3$)$_4$(OH$_2$)$_2$]$_2$(SO$_4$)$_3$·3H$_2$O	−0.48$_5$	−0.40$_2$
trans-[Co en$_2$(NH$_3$)$_2$]Cl$_3$·H$_2$O	−0.45	−0.31
cis-[Co en$_2$(NH$_3$)$_2$](ClO$_4$)$_3$	−0.45	−0.31
[Co(NH$_3$)$_6$](ClO$_4$)$_3$	−0.43$_8$	−0.23$_5$
trans-[Co en$_2$(NO$_2$)$_2$]Cl	−0.26	−0.27***
trans-[Co(NH$_3$)$_4$(NO$_2$)$_2$]ClO$_4$	−0.20$_7$**	−0.21
cis-[Co en$_2$(NO$_2$)$_2$]ClO$_4$	−0.25	−0.24***
cis-[Co(NH$_3$)$_4$(NO$_2$)$_2$]ClO$_4$	−0.04$_3$**	−0.04$_8$

The data for the cobalt(III) complexes of bisethylenediamine series were quoted from N. Maki, Y. Shimura and R. Tsuchida, This Bulletin, **32**, 150 (1959). The concentration of complex: 0.001 gram complex ion per litre. Potential unit: V. vs. S.C.E.

* Maximum wave

** The data quoted from J. B. Willis, J. A. Friend and D. P. Mellor, *J. Am. Chem. Soc.*, **67**, 1680 (1945).

*** The data adopted from H. F. Holtzclaw, Jr. and D. P. Sheetz, ibid., **75**, 3053 (1953).

**** The data obtained in the presence of 0.0016% Tween-80.

diaquobisethylenediaminecobalt(III) complex[1] and could not be diminished only by the removal of the oxygen dissolved in solution. In perchloric acid, on the other hand, the first wave becomes steeper as is shown in Fig. 3. The reason for this is considered to be quite similar to the case of *cis*-diaquobisethylenediaminecobalt(III) complex. Namely, in neutral aqueous solution, the hydroxytetramminecobalt(III) ions are formed by the following ligandolysis.

$$[Co(NH_3)_4(OH_2)_2]^{3+} \rightleftarrows [Co(NH_3)_4(OH_2)(OH)]^{2+} + H^+$$

$$[Co(NH_3)_4(OH_2)(OH)]^{2+} \rightleftarrows [Co(NH_3)_4(OH)_2]^{+} + H^+$$

The monohydroxymonoaquo complex ions formed here polymerize to the various kinds of the polynuclear cobalt(III) complex with the lapse of time, as was verified by the spectrochemical studies of Rasmussen et al.[23]

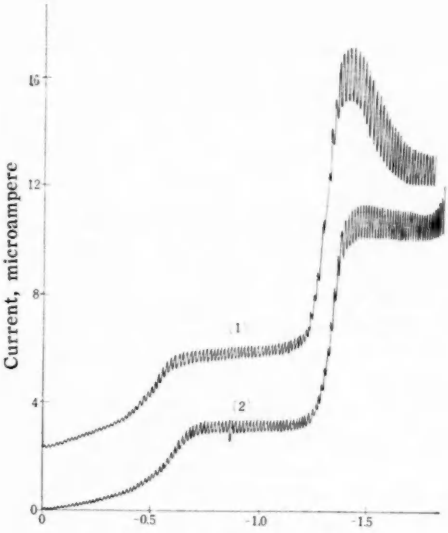
For instance,

$$2\ cis\text{-}[Co(NH_3)_4(OH_2)(OH)]^{2+} \rightarrow \left[(NH_3)_4Co\begin{matrix}OH\\OH\end{matrix}Co(NH_3)_4\right]^{4+} + 2H_2O$$

Accordingly, in neutral solution the several kinds of these cobalt(III) complexes having similar structures are considered to be reduced almost at the same time.

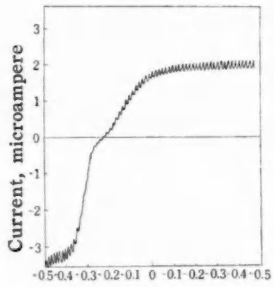
The above mechanism well explains the fact that the overlapped waves of small slope are obtained for the diaquotetramminecobalt(III) complex. In perchloric acid, on the other hand, the above equilibrium is markedly shifted to the left hand due to the presence of an overwhelming hydrogen ion. Hence, the polymerization is quite inhibited and only the original ion is present in solution. Consequently, the wave of steep slope was obtained.

23) S. E. Rasmussen and J. Bjerrum, *Acta Chem. Scand.*, **9**, 735 (1955).



Applied potential, volt vs. S.C.E.

Fig. 2. The polarograms of *cis*-diaquotetramminecobalt(III) complex, $[Co(NH_3)_4(OH_2)_2](SO_4)_3 \cdot 3H_2O$, obtained at the concentration of 0.001 gram complex ion per litre in 0.5 F K_2SO_4 solution.
1. In the absence of the maximum suppressor.
2. In the presence of 0.0032% Tween-80.
Sensitivity: 0.08 μA/mm. Damping: 200.



Applied potential, volt vs. S.C.E.

Fig. 3. The polarogram of *cis*-diaquotetramminecobalt(III) ion, $[Co(NH_3)_4(OH_2)_2]^{3+}$, obtained in 1 F perchloric acid at the concentration of 0.001 gram complex ion per litre.

The wave of *cis*- or *trans*-dichlorotetramminecobalt(III) ion which appeared at around -0.42 V. (vs. S.C.E.) is considered to correspond to the reduction of the aquated species such as $[Co(NH_3)_4(OH_2)Cl]^{2+}$ and $[Co(NH_3)_4(OH_2)_2]^{3+}$, since the half-wave potential is in proximity to that of diaquotetramminecobalt(III) ion. ($E_{1/2} = -0.40_2$ V. vs. S.C.E. in 0.1 F KCl). Judging from the wavelet, the reduction wave of the original ion is believed to be in the positive region of potential.

As to the wave of diiodatotetramminecobalt(III) complex, $[Co(NH_3)_4(IO_3)_2]IO_3 \cdot HIO_3$, the half-wave potential of the first wave is in the positive region of potential and the second wave is covered by the reduction wave of the hydrogen ion liberated from iodic acid.

Summary

1. All the cobalt(III) complexes of tetrammine series, $[Co(NH_3)_4X_2]$ or $[Co(NH_3)_4Y]$, were reduced irreversibly in two steps at the dropping mercury electrode. The first wave, corresponding to a gain of one electron, represents the reduction of Co(III)→Co(II) and the second, corresponding to two electrons, represents the reduction of Co(II)→Co(0).

2. The polarographic stability of the cobalt(III) complexes of tetrammine series are ranked in the following order of the ligand; for the complexes of $[Co(NH_3)_4X_2]$ type,

IO_3^-, $Cl^- < NO_2^- < NH_3 < OH_2 < SO_3^{2-}$

(supporting electrolyte; 0.5 F K_2SO_4),

and for the complexs of $[Co(NH_3)_4Y]$ type,

$leuc^- < ox^{2-} < alan^- < CO_3^{2-} < gly^- < en$

(supporting electrolyte; 0.5 F K_2SO_4).

3. The half-wave potentials of the reduction step of Co(III)→Co(II) for all the tetrammine cobalt(III) complexes exhibit always more positive values than those of the corresponding bisethylenediamine cobalt(III) complexes.

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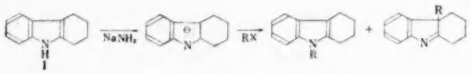
Alkylation of 2,3-Dimethylindole in Liquid Ammonia

By Masao NAKAZAKI

(Received February 9, 1959)

In the previous paper[1], formation of both 9-alkyltetrahydrocarbazoles (IIa, b, c) and 11-alkyltetrahydrocarbazolenines (IIIa, b, c) by the alkylation of tetrahydrocarbazole(I) in liquid ammonia with sodium amide and alkyl halides was reported. But, when isopropyl iodide was employed as alkylation reagent, 11-isopropyltetrahydrocarbazolenine (IIId) was a sole product isolated. These 11-alkyltetrahydrocarbazolenines could be also prepared by the Grignard synthesis, contrary to the negative result of Witkop[2].



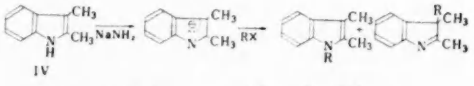
II a, R=CH_3 III a, R=CH_3
b, R=CH_2-CH=CH_2 b, R=CH_2-CH=CH_2
c, R=$CH_2C_6H_5$ c, R=$CH_2C_6H_5$
d, R=$CH(CH_3)_2$

When these experiments had been completed, Patts and Saxton[3] published a paper in which they reported formation of *N*-methyl derivatives in excellent yield from various indole derivatives by the alkylation with sodium amide and methyl iodide in liquid ammonia.

Beside indole itself, all compounds they tried were 2- or 3-monosubstituted indole, and no 2,3-disubstituted indole was subjected to their alkylation method.

Since tetrahydrocarbazole is a 2,3-disubstituted indole, and affords both 9- and 11-alkyl derivatives by the alkylation in liquid ammonia, 2,3-dimethylindole can be expected to give indolenine derivatives by this method.

When the same procedure used in the alkylation of tetrahydrocarbazole was employed, 2,3-dimethylindole gave *N*-methyl derivative (Va) accompanied by a small amount of 2,3,3-trimethylindolenine (VIa), but using allyl bromide and benzyl chloride there were found *N*-alkyl (Vb, c) and indolenine derivatives (VIb, c) in about the same amount.



IV

V a, R=CH_3 VI a, R=CH_3
b, R=$CH_2C_6H_5$ b, R=$CH_2C_6H_5$
c, R=CH_2-CH=CH_2 c, R=CH_2-CH=CH_2
d, R=$CH(CH_3)_2$

Isopropyl bromide failed to afford *N*-isopropyl derivative and a small amount of 2,3-dimethyl-3-isopropylindolenine (VId) was the only prduct isolated. These results are exactly parallel to the one observed in the case of the alkylation of tetrahydrocarbazole in liquid ammonia.

The structures of all indolenine compounds provided by the alkylation in liquid

TABLE I

	Methyl iodide		Benzyl chloride		Allyl bromide		Isopropyl bromide	
Product	Va	VIa	Vb	VIb	Vc	VIc	*	VId
M. p.			59～ 60	48～ 49				
B. p. (mmHg)	117～120 (6)	113 (21)	110～115 (1.5)		159～161 (16)	128～132 (12)		100～110 (11)
M. p.** of picrate	148～149 B	158～160 Y	98～ 99 B	138～141 Y	86 B	156～157 Y		173～174 Y

* Could not be obtained by the alkylation in liquid ammonia or by the Grignard synthesis.

** Picrates of *N*-alkyl derivatives are brown black needles (B), and picrates of indolenines are yellow (Y).

1) M. Nakazaki and S. Isoe, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **76**, 1159 (1955).
2) B. Witkop, *J. Am. Chem. Soc.*, **72**, 614 (1950).
3) K. T. Patts and J. E. Saxton, *J. Chem. Soc.*, **1954**, 2641. In our independent work, indole was found to give *N*-benzyl and *N*-allylindole in liquid ammonia with sodium amide and benzyl chloride and allyl bromide, respectively.

ammonia, were confirmed by the comparison with the specimens prepared by the Grignard synthesis, and their properties were shown in Table I, together with the one of *N*-alkyl-2,3-dimethylindoles.

Since 2,3-disubstituted indoles, as this experiment clearly shows, must be expected to give a considerable amount of indolenine derivatives even when methyl iodide is employed in the alkylation in liquid ammonia, adequate caution should be paid at the application of this alkylation method to the structure determination or the synthesis of indole alkaloids and the related compounds[4].

Experimental

N-Methyl-2,3-dimethylindole (Va) and 2,3,3-Trimethylindolenine (VIa). — *Alkylation in liquid ammonia.*—To 150 cc. of liquid ammonia collected in a three-necked flask chilled in a dry ice-acetone bath, 0.05 g. of ferric nitrate was added followed by the addition of 0.8 g. of sodium. After the blue color disappeared, a solution of 5 g. of 2,3-dimethylindole in 20 cc. of ether was added dropwise with stirring. After a mixture of 5 g. of methyl iodide and 5 cc. of ether was added over 20 min., the cooling bath was removed and the flask was allowed to stand overnight at room temperature to evaporate the ammonia off. Water was added to the residue left in the flask, and the oil separated was extracted with ether.

The ether extract was washed with water to neutral, and dried over anhydrous magnesium sulfate. After removal of the solvent, yellow residue was distilled under reduced pressure.

A forerun (1 g.) which boiled below 117°C at 6 mmHg and had a smell reminiscent of jasmine was dissolved in ether.

The basic fraction extracted with 4 N hydrochloric acid was liberated by the addition of 2 N sodium hydroxide solution and taken up in ether. An pale yellow oil (0.5 g.) obtained after removal of the ether, was converted into picrate which melted at 158°C after recrystallization from ethanol. The mixed melting point with the picrate of 2,3,3,-trimethylindolenine (m. p. 158~160°C) prepared by the Grignard synthesis was 158~161°C.

The main fraction boiling at 117~120°C/6 mmHg, weighed 3.2 g. (58% yield).

Anal. Found: C, 82.80; H, 8.29; N, 8.80. Calcd. for $C_{11}H_{13}N$: C, 82.97; H, 8.24; N, 8.80%.

The picrate was recrystallized from benzene to yield brown-black needles, m. p. 148~149°C. (literature[5]): m. p. 150°C). The mixed m. p. with the picrate of 2,3-dimethylindole (m. p. 152~153°C) was 140~143°C.

Grignard synthesis.—2,3,3-Trimethylindolenine was prepared following Hoshino's procedure[6], b. p. 113°C/21 mmHg. The picrate was recrystallized to give yellow needles melting at 158~160°C (literature[6]: m. p. 160~161°C).

N-Benzyl-2,3-dimethylindole (Vb) and 2,3-Dimethyl-3-benzylindolenine (VIb).—*Alkylation in liquid ammonia.*—Into a solution of sodium amide prepared from 200 cc. of liquid ammonia, 0.05 g. of ferric nitrate and 0.78 g. of sodium, a mixture of 5 g. of dimethylindole in 10 cc. of ether was added followed by the addition of 4 g. of benzyl chloride in 10 cc. of ether with stirring. After being kept overnight at room temperature in order to evaporate the ammonia, the residue was extracted with ether, and a basic fraction was extracted with 2 N hydrochloric acid. The basic fraction was liberated by the addition of 4 N sodium hydroxide solution to the hydrochloric acid solution, and extracted with ether. The ether layer, after being washed with water and dried, was evaporated to afford a viscous liquid which solidified gradually (1.80 g.). A small amount was sublimed to give crystals, m. p. 48~49°C. This was found identical with 2,3-dimethyl-3-benzylindolenine prepared by the Grignard synthesis[7] by mixed m. p. determination.

The picrate was recrystallized from ethanol to yield yellow needles, m. p. 138~140°C. The mixed melting point with the picrate prepared from the indolenine synthesized by the Grignard synthesis[7] was 138~141°C.

The natural fraction. — The ether layer freed of the indolenine was washed with water and dried. The solvent was removed to give 5.74 g. of a brown viscous liquid which solidified when allowed to stand at room temperature overnight. After 1.4 g. of dimethylindole (m. p. 94~97°C. picrate: m. p. 153~154°C, identified by mixed m. p. determinations) was recovered by sublimation at 3 mmHg, the residue was distilled in vacuo. A pale yellow fraction boiling at 110~115°C/1.5 mmHg was collected (1.7 g.) and recrystallized from methanol to give large needles, m. p. 59~60°C.

Anal. Found: C, 86.74; H, 7.32. Calcd. for $C_{17}H_{17}N$: C, 86.77; H, 7.28%.

The picrate was recrystallized to give brown black needles, m. p. 98~99°C.

Anal. Found: C, 59.79; H. 4.60; N, 12.20. Calcd. for $C_{23}H_{20}O_7N_4$: C, 59.88; H, 4.34; N, 12.06%.

N-Allyl-2,3-dimethylindole (Vc) and 2,3-Dimethyl-3-allylindolenine (VIc).—*Alkylation in liquid ammonia.* — To a solution of sodium amide prepared from 200 cc. of liquid ammonia, 0.05 g. of ferric nitrate and 1.2 g. of sodium, 7.0 g. of dimethylindole was added with 20 cc. of ether followed by the addition of a mixture of 7.7 g. of allyl bromide and 10 cc. of ether. The basic and neutral fractions were separated by the procedure described above.

4) M. F. Bartlett, D. F. Dickel and W. I. Taylor., *J. Am. Chem. Soc.*, **80**, 126 (1958), in which is obtained the only *N*-methylibogaine from iboganine (a 2,3-disubstituted indole) following the procedure of Patts and Saxton.

5) J. Degen, *Ann.*, **236**, 162 (1886).

6) T. Hoshino, ibid., **500**, 35 (1932).

7) M. Nakazaki, S. Isoe and K. Tanno, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **76**, 1262 (1955).

The basic fraction boiled at 128~132°C/12 mmHg and weighed 3.82 g. This 2,3-dimethyl-3-allylindolenine (VIc) was very sensitive to air oxidation and rapidly turned brown at the surface, but was able to be kept a little while in a refrigerator in a sealed bottle.

Anal[8]. Found: C, 82.75; H, 8.32; N, 7.06. Calcd. for $C_{13}H_{15}N$: C, 84.28; H, 8.16; N, 7.56%.

The picrate was recrystallized from ethanol to give yellow needles, m. p. 156~157°C, and it was found identical with the picrate of 2,3-dimethyl-3-allylindolenine prepared by the Grignard synthesis (vide infra).

The neutral fraction boiled at 159~160°C/16 mmHg and weighed 3.22 g.

Anal. Found: C, 84.11; H, 8.38; N, 7.35. Calcd. for $C_{13}H_{15}N$: C, 84.28; H, 8.16; N, 7.56%.

The picrate was recrystallized from ethanol to give brown black needles, m. p. 86°C.

Anal. Found: C, 54.85; H, 4.34; N, 13.37. Calcd. for $C_{19}H_{18}O_7N_4$: C, 55.07; H, 4.38; N, 13.52%.

Grignard synthesis.—To a Grignard compound prepared from 11.1 g. of methyl iodide and 1.9 g. of magnesium in 20 cc. of ether, a solution of 7.0 g. of dimethylindole in 20 cc. of ether was added dropwise over a period of 25 min. After generation of methane subsided, 7.7 g. of allyl bromide was added slowly over 20 min., and stirred for one additional hour. The ether layer was separated, after the Grignard complex was decomposed by the addition of 4 cc. of acetic acid with 15 cc. of water, and the aqueous layer was extracted thoroughly with ether. The combined ether extracts were shaken with 2 N hydrochloric acid to extract the basic fraction.

The oil which separated from the hydrochloric acid solution by being made alkaline was extracted with ether. After removal of the solvent, the residual liquid was distilled in vacuo to give a liquid which had a camphor-like smell, b. p. 80~90°C/2 mmHg, weighed 4.05 g.

2,3-Dimethyl-3-allylindolenine was found quickly to turn brown in color by air oxidation.

Anal[8]. Found: C, 82.86; H, 8.41; N, 6.95. Calcd. for $C_{13}H_{15}N$: C, 84.28; H, 8.16; N, 7.56%.

The picrate was recrystallized from ethanol to give yellow crystals, m. p. 157~158°C.

Anal. Found: C, 55.22; H, 4.60; N, 13.54. Calcd. for $C_{19}H_{18}O_7N_4$: C, 55.07, H, 4.38; N, 13.52%.

2,3-Dimethyl-3-isopropylindolenine (VId). —*Alkylation in liquid ammonia.*— To a solution of sodium amide prepared from 250 cc. of liquid ammonia, 0.1 g. of ferric nitrate and 1.5 g. of sodium in a 3-necked flask chilled in a dry ice-acetone bath, 7.0 g. of dimethylindole was added with 20 cc. of ether, followed by the addition of 7.5 g. of isopropyl bromide over 20 min. with stirring. The cooling bath was removed and the reaction mixture was allowed to stand at room temperature overnight to evaporate the ammonia. Following the same procedure described above, the basic and neutral fractions were separated. The basic fraction boiled at 100~110°C/11 mmHg, weighed 0.2 g. This compound was noticed to have a characteristic indolenine smell.

Anal. Found: C, 82.62; H, 9.59; N, 7.92. Calcd. for $C_{13}H_{17}N$: C, 83.37; H, 9.15; N, 7.48%.

The picrate was recrystallized to give yellow crystals, m. p. 173~174.5°C.

Anal. Found: C, 55.00; H, 5.08; N, 13.92. Calcd. for $C_{19}H_{20}O_7N_4$: C, 54.80; H, 4.84; N, 13.46%.

The neutral fraction weighed 7.9 g., and from it 4.6 g. of dimethylindole was recovered by sublimation. But attempts to isolate *N*-isopropyl derivative from the viscous residue in the form of picrate failed, and the picrate of dimethylindole was the only material traceable.

Grignard synthesis.— To a Grignard solution prepared from 1.9 g. of magnesium and 11.1 g of methyl iodide in 20 cc. of ether, a mixture of 7.0 g. of dimethylindole in 10 cc. of ether was added dropwise.

After the evolution of methane subsided, 7.9 g. of isopropyl bromide was added over a period of 30 min. with stirring and cooling in an ice bath. After being kept at room temperature for 2 hr., the Grignard complex was decomposed by the addition of 4 cc. of acetic acid and 15 g. of ice. The basic and neutral fractions were separated by the same procedure described above.

The basic fraction was distilled in vacuo to give a liquid which boiled at 75~90°C/10 mmHg. Yield, 0.7 g.

The picrate was recrystallized to afford yellow crystals, m. p. 173~175°C which melted at 172~173°C when admixed with the picrate of 2,3-dimethyl-3-isopropylindolenine prepared by the alkylation of dimethylindole in liquid ammonia. From the neutral fraction, only dimethylindole was recovered.

The authors is very grateful to Mr. Muneo Sato for his enthusiastical technical assistance.

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8) This rather poor result may be due to the sensitivity of the indolenine to air oxidation.

Benzoylation of 1,3-Diazaazulene[1]

By Ichiro MURATA

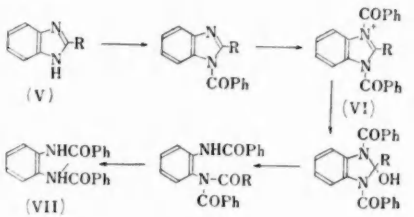
(Received February 6, 1959)

In 1949, Nozoe[2] predicted the possibility that the so-called 2-aminotropoimine and azaazulenes, which may be considered as the nitrogen homolog of tropolone and azulene respectively, are stable enough to exist. Later studies have confirmed their presence by the syntheses of azaazulenes such as 1-azaazulene (I)[3] and 1,3-diazaazulene (II)[4].

(I) (II) (III) (IV)

However, the only derivative of 2-aminotropoimine (III) known to date is 2,5-diaminotropoimine (IV)[5] obtained by the reduction of 5-nitrosotropolone dioxime (*p*-tropoquinone trioxime)[6].

In a sense, 1,3-diazaazulene (II) may be considered as a seven-membered ring homolog of benzimidazole (V). From such a view point, the cleavage reaction of an imidazole ring by the Schotten-Baumann method, known as the Bamberger reaction[7,8] in imidazole compounds, was applied to II.



Scheme 1.

The Bamberger reaction is considered to poceed as indicated in Scheme 1, starting with benzoylation, followed by the formation of a quaternary base (VI) by the presence of excess benzoyl chloride and the cleavage of the base by the action of alkali hydroxide, forming *o*-phenylenediamine dibenzoate (VII)[8].

II differs from the imidazole ring in not possessing an N-H group that could be benzoylated. However, since II easily forms a methiodide[4], the possibility of its ring fission may be considered and examination of this reaction was made.

A solution of II dissolved in 4 molar equivalents of sodium hydroxide solution, and chilled in ice, was added with 4 molar equivalents of benzoyl chloride, the mixture was shaken thoroughly, and allowed to stand overnight. This was extracted with chloroform and the brown oil obtained from the extract was separated and purified by alumina chromatography, from which yellow scales (VIII), m. p. 157 ~158°C, and pale yellow needles (IX), m. p. 94~95°C, were obtained besides recovery of the starting II.

By exactly the same procedure, the reaction of 6 molar equivalents of sodium hydroxide and 4 molar equivalents of benzoyl chloride gave a small amount of pale yellow prisms (X), m. p. 158°C, besides VIII and recovery of II.

When this reaction was carried out at 70~72°C, the kind and amount of the products obtained were different, as indicated in Table I.

The reaction of II and benzoyl chloride

TABLE I. REACTION OF 1,3-DIAZAAZULENE AND BENZOYL CHLORIDE

Molar ratio			Temp.	Product (%)			
II	NaOH	C_6H_5COCl	(°C)	VIII	IX	X	II
1	4	4	0	25	30	—	37
1	6	4	0	30	—	5	40
1	4	4	70~72	—	60	—	15
1	6	4	70~72	—	—	62	14

1) Presented at the Local Meeting of Tohoku District of the Chemical Society of Japan, held at Yonezawa, June 25, 1956.

2) T. Nozoe, *Science of Drugs* (*Yakugaku*), **3**, 191 (1949); T. Nozoe, *Science Repts. Tohoku Univ.*, **I**, **34**, 225 (1950).

3) T. Nozoe, S. Seto, S. Matsumura and T. Terasawa, *Chem. and Ind.*, **1954**, 1357.

4) T. Nozoe, T. Mukai and I. Murata, *J. Am. Chem. Soc.*, **76**, 3352 (1954).

5) T. Nozoe, M. Sato, S. Ito, K. Matsui and T. Matsuda, *Proc. Japan Acad.*, **29**, 565 (1953); T. Nozoe and S. Ito, unpublished data.

6) T. Nozoe and S. Seto, *Proc. Japan Acad.*, **27**, 188 (1951).

7) E. Bamberger, *Ann.*, **273**, 267 (1893); E. Bamberger, B. Berle, ibid., **273**, 342 (1893).

8) A. Weissberger, "The Chemistry of Heterocyclic Compounds, Imidazole and its Derivatives", Part I, Interscience Publishers, New York (1953), p. 48, 273.

afforded, according to conditions of the reaction, VIII and IX or X. Examinations were made on the structure of these three products.

VIII and X show the same melting point but a distinct depression of the melting point occurs on their admixture and they show different degrees of solubility, color, and crystal form. The ultraviolet absorption spectra[9] of the two compounds, shown in Fig. 1, are also entirely different. Elementary analytical values of X correspond to the molecular formula of $C_{14}H_{10}N_2$, not containing any oxygen. It easily forms a picrate of m.p. 210°C, a styphnate of m.p. 231°C (decomp.), and a hydrochloride of m.p. 210°C (decomp.), whose analytical values also agree with those calculated for a salt of the foregoing composition.

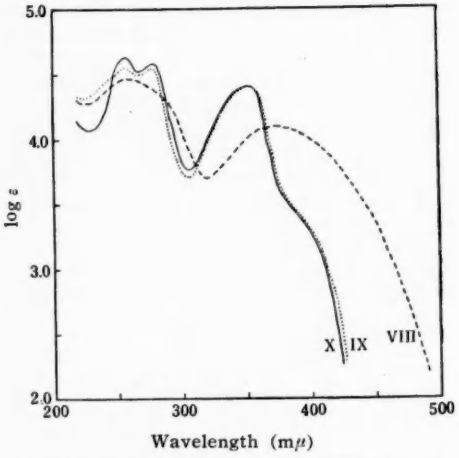


Fig. 1. U.V. absorption spectra of VIII, IX and X in methanol.

The infrared absorption spectrum[10] of X (Fig. 2) exhibits an absorption band at 1604 cm^{-1}, corresponding to the C=N stretching vibration or ring vibration (1602 cm^{-1}) in 1,3-diazaazulene, and absorption bands at 717 and 686 cm^{-1} due to the C–H out-of-plane vibration of mono-substituted benzene. These facts suggest that X is a phenyl derivative of II.

Oxidation of X with potassium dichromate in diluted sulfuric acid affords 2-phenylimidazole-4,5-dicarboxylic acid(XI)[11] of m.p. 264°C (decomp.), and its decarboxylation gives 2-phenylimidazole (XII)[11] of m.p. 143°C, which showed no depression on admixture with XII synthesized from tartaric acid. The ultraviolet absorption spectra of these two compounds were also identical. It follows, therefore, that the structure of X is 2-phenyl-1,3-diazaazulene.

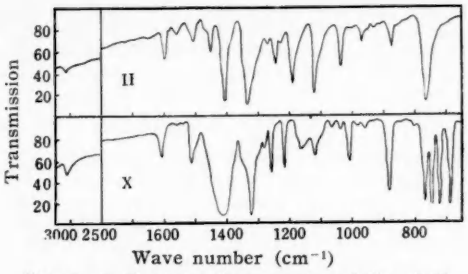


Fig. 2. I.R. absorption spectra of II and X in KBr.

IX is converted into X merely by mild treatment with dilute alkali and liberates one molar equivalent of benzoic acid during this course. The ultraviolet spectrum (Fig. 1) of IX is almost identical with that of X except for the absorption at around 230 mμ[12]. Since the heating of X with an equivalent amount of benzoic acid in ethanol results in quantitative formation of IX and from the analytical

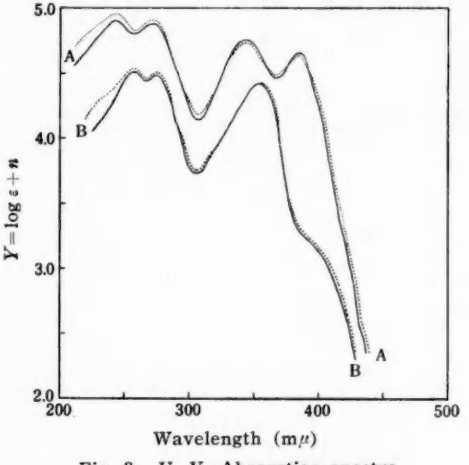


Fig. 3. U.V. Absorption spectra
—— X ····· VIII
A, in 0.1N HCl ($Y=\log\varepsilon+0.5$)
B, in 0.1N NaOH ($Y=\log\varepsilon+0$)

9) Measured by the Beckman Model DU Spectrophotometer.

10) I.R. spectra are measured using Perkin-Elmer Model 21 double beam spectrophotometer by Mr. Y. Ikegami of this Institute, to whom the author is deeply indebted.

11) R. G. Fargher and F. L. Pyman, *J. Chem. Soc.*, **115**, 217 (1919).

12) This is considered to have appeared by the overlapping of the K-band of benzoic acid. Cf. A. E. Gillam and E. S. Stern, "An Introduction to Electronic Absorption Spectroscopy in Orgaic Chemistry", Edward Arnold Publishers, London (1954), p. 126.

values of IX, it is assumed that IX is a benzoic acid salt of X.

Analytical values of VIII agree with $C_{21}H_{16}O_2N_2$. Its mild treatment with dilute acid or alkali affords X from the basic portion and one molar equivalent of benzoic acid from the acid portion. The ultraviolet spectrum of VIII (Fig. 1) shows an entirely different curve from those of IX and X, but its spectrum in acid and alkaline solvents (Fig. 3) shows a curve extremely similar to the absorption of X in acid and alkaline media with the exception of the absorption at around 230 mμ[12].

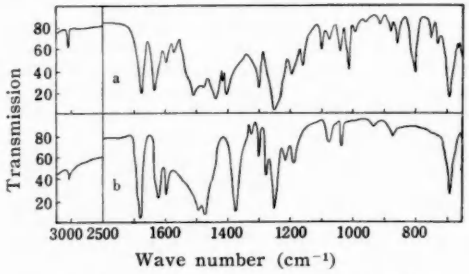
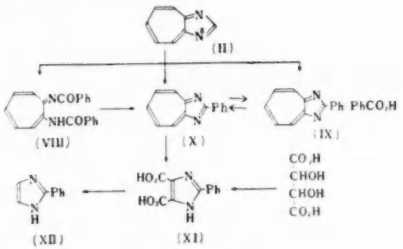


Fig. 4. I. R. absorption spectra of VIII.
a, in KBr-pellet; b, in CCl_4 soln.

In the infrared absorption spectrum of VIII (Fig. 4), there are absorptions considered to be the C=O stretching vibration of secondary amide[13] at the wave number[15] of 1683 (1676), the N–H deformation vibration at 1492 (1515), the N–H strectching vibration at (3290), and the C=O stretching vibration of tertiary amide at 1622 (1630).



Scheme 2.

The foregoing results suggest that VIII is 2-aminotropoimine dibenzoate formed by the ring-cleavage of II. These changes are presented in Scheme 2.

Attempts were made to remove the benzoyl group from VIII by hydrolysis and to obtain the parent structure, 2-aminotropoimine (III), but the attempts failed because of the extreme facility with which VIII underwent cyclization[16] and its facile conversion to X under the conditions for hydrolysis.

Experimental[17]

Reaction of 1,3-Diazaazulene (III) and Benzoyl Chloride.—a) To a solution of 300 mg. (2.3 mmol.) of II dissolved in a solution of 370 mg. (9.2 mmol.) of sodium hydroxide in 8 cc. of water, 1.29 g. (9.2 mmol.) of benzoyl chloride was added in one lot, under ice cooling, and the mixture was stirred thoroughly. This treatment is accompanied by a considerable generation of heat and the mixture must be chilled efficiently. When yellowish brown clay-like substance began to separate out on the wall of the vessel, the mixture was allowed to stand overnight and extracted with chloroform, from which 1.02 g. of brown oily substance was obtained. This oil was dissolved in 2 cc. of mixture of benzene and petroleum ether (1 : 1), and the solution was passed through a column (10×150 mm.) of alumina. The column was eluted with petroleum ether and 80 mg. of yellow crystals, m. p. 146~151°C, was obtained. Four recrystallizations from ethanol afforded 2-aminotropoimine dibenzoate (VIII) as yellow scaly crystals, m. p. 157~158°C.

Further elution of the alumina column with mixture of benzene and petroleum ether (1 : 1) afforded 90 mg. of pale yellow oil which was crystallized from cyclohexane to crystals of m. p. 91~92°C. Recrystallization from benzene-cyclohexane mixture afforded 2-phenyl-1,3-diazaazulene benzoic acid salt (IX) as pale yellow needles, m. p. 94~95°C.

Further elution of the column with benzene, followed by elution with ethanol, gave dark brown oil from both. These products were derived to respective picrates and decomposed by dilute hydrochloric acid, from which 110 mg. of unchanged II was recovered.

b) To a solution of 500 mg. (3.8 mmol.) of II dissolved in a solution of 915 mg. (22.8 mmol.) of sodium hydroxide in 16 cc. of water, 2.13 g. (15.2 mmol.) of benzoyl chloride was added and reacted as in a). Purification through a column (10×180 mm.) of alumina was carried out similarly and 140 mg. of VIII from the fraction eluted with petroleum ether and 25 mg. of yellow crystals,

13) Absorption of 2-benzoylaminotropone[14] as the secondary amide with unsaturated seven-membered ring was as follows: 1685 (1678), 1502 (1513), 3270 (3275); these values were read by the author.

14) T. Nozoe, S. Seto, H. Takeda, S. Morosawa and K. Matsumoto, *Science Repts. Tohoku Univ.*, **I**, **36**, 126 (1952).

15) Measurements were made by the KBr-pellet method. Values in parentheses are of those measured as CCl_4 solution.

16) It has been also known that *o*-phenylenediamine dibenzoate also undergoes facile dehydration and cyclization to 2-phenylbenzimidazole. Cf. O. Gerngross, *Ber.*, **46**, 1913 (1913).

17) All melting points are uncorrected. Petroleum ether used in this work was of b. p. 40~60°C. The microanalyses were carried out by Mr. S. Ohyama and Miss A. Iwanaga, to whom the author's deep gratitude is hereby expressed.

m. p. 142~153°C, from a fraction eluted with benzene-petroleum ether were obtained. Recrystallization of the latter from benzene-petroleum ether mixture afforded 2-phenyl-1, 3-diazaazulene (X) as yellow prisms, m. p. 158~159°C.

c) A solution of 830 mg. (6.34 mmol.) of II dissolved in a solution of 1.02 g. (25.5 mmol.) of sodium hydroxide in 26 cc. of water was heated to 70~72°C on a water bath and 3.57 g. (25.5 mmol.) of benzoyl chloride was added in one lot with stirring. The mixture was maintained at this temperature for 1 hr., cooled, and extracted with chloroform. The oily substance obtained from this extract was purified by chromatography and 510 mg. of IX was obtained besides recovery of 155 mg. of II.

d) A solution of 850 mg. (6.5 mmol.) of II dissolved in a solution of 1.56 g. (39 mmol.) of sodium hydroxide in 27 cc. of water was reacted with 3.64 g. (26 mmol.) of benzoyl chloride as in c) and 520 mg. of X and 120 mg. of II were obtained.

2-Aminotropoimine Dibenzoate (VIII).—*Anal.* Found: C, 76.89; H, 4.80; N, 8.76. Calcd. for $C_{21}H_{16}O_2N_2$: C, 76.81; H, 4.91; N, 8.53%.

2-Phenyl-1, 3-diazaazulene Benzoic Acid Salt (IX).—*Anal.* Found: C, 76.28; H, 4.71; N, 8.56. Calcd. for $C_{14}H_{10}N_2 \cdot C_7H_6O_2$: C, 76.81; H, 4.91; N, 8.53%.

2-Phenyl-1, 3-diazaazulene (X).—*Anal.* Found: C, 78.05; H, 5.06; N, 13.37. Calcd. for $C_{14}H_{10}N_2 \cdot \frac{1}{2} H_2O$: C, 78.12, H, 5.15; N, 13.02%.

Found (in a sample dried over P_2O_5 at 50°C/10 mmHg): C, 81.28; H, 4.95; N, 13.82. Calcd. for $C_{14}H_{10}N_2$: C, 81.53; H, 4.89; N, 13.58%.

a) Hydrochloride of X: Pale yellow prisms, m. p. 210°C (blacken) as recrystallized from ethanol.

Anal. Found: N, 11.47. Calcd. for $C_{14}H_{10}N_2 \cdot HCl$: N, 11.53%.

b) Picrate of X: Pale yellow, silky needles, m. p. 209~210°C, as recrystallized from water.

Anal. Found: C, 55.12; H, 3.43; N, 16.17. Calcd. for $C_{14}H_{10}N_2 \cdot C_6H_3O_7N_3$: C, 55.18; H, 3.01; N, 16.09%.

c) Styphnate of X: yellow silky needles, m. p. 231°C (decomp.), as recrystallized from 50% ethanol.

Anal. Found: C, 52.87; H, 3.24; N, 15.31. Calcd. for $C_{14}H_{10}N_2 \cdot C_6H_3O_8N_3$: C, 53.22; H, 2.90; N, 15.52%.

d) Benzoic acid salt (IX) of X: A solution of 50 mg. of X and 20 mg. of benzoic acid dissolved in 1 cc. of ethanol was heated for a few minutes, ethanol was evaporated, and the residue was recrystallized from benzene-petroleum ether mixture to pale yellow needles, m. p. 93~94°C, which showed no depression on admixture with IX.

Oxidation of X with Potassium Dichromate.—A solution of 150 mg. of X and 490 mg. of potassium dichromate dissolved in 12 cc. of 6 N sulfuric acid was heated on a water bath for 45 min. and the mixture was allowed to stand for 3 days at room temperature. The crystals that separated out were collected by filtration and 55 mg. of XI, m. p. 263~264°C (decomp.), was obtained. This XI was sublimed under diminished pressure to effect decarboxylation and 30 mg. of colorless crystals, m. p. 138~140°C, was obtained which showed no depression in the melting point on admixture with 2-phenylimidazole (XII), synthesized from tartaric acid[18].

Hydrolysis of VIII.—a) A mixture of 200mg. of VIII in 1.5 cc. of 2 N sulfuric acid was heated on a water bath for a few minutes, by which time the crystals dissolved to form an orange solution. This solution was extracted with chloroform and 50 mg. of crystals; m. p. 111~120°C, was obtained. Recrystallization from petroleum ether raised the melting point to 119~120°C, undepressed by admixture with benzoic acid. The aqueous layer separated after chloroform extraction was made weakly alkaline with sodium hydrogen carbonate and extracted with chloroform, from which 125 mg. of crystals melting at 156~157°C, identified with X, was obtained.

b) A mixture of 50 mg. of VIII dissolved in 1 cc. of ethanol and 0.5 cc. of 2 N sodium hydroxide solution was refluxed on a water bath for 5 min., ethanol was evaporated, and the residual solution was diluted with water. This was extracted with chloroform and 20 mg. of X was obtained from the extract. Extraction of the aqueous layer after acidification afforded 10 mg. of benzoic acid.

The author takes this opportunity to express his deep gratitude to Professor Tetsuo Nozoe for his unfailing guidance and to Assistant Professor Toshio Mukai for much helpful advice.

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Katahira-cho, Sendai

18) Ultraviolet absorption spectra of the sample and synthesized product were in good agreement, both showing λ_{max}^{MeOH} 269 mμ (log ε 4.20) and λ_{min}^{MeOH} 230 mμ (log ε 3.37).

The Kinetic Study of Surface-chemical Reactions at Extremely Low Pressures. II. The Thermal Reaction between Water Vapor and a Tungsten Filament. Part II

By Takuya HAMAMURA

(Received August 15, 1958)

It has been shown previously[1] by a hot filament method that the major part of water molecules impinging on the hot surface of tungsten filament rebound without reaction even at high temperatures. These results, however, were not free from the end effect of the filament, since it was kept cooler at the both ends, where it was joined with leads which were much thicker than the filament and hence practically not heated at all by an electric current; the reaction probability* determined directly from the observed rate of reaction is, in consequence, an average one being smaller than that at the middle portion. The present paper is concerned with the elimination of the effect of the above-mentioned end losses.

Several devices[2] have been reported for the elimination of end losses, e. g., to heat the leads with auxiliary heaters attached to them or to heat the filament from outside of the vessel by an electric furnace, but the former is complicated in structure and the latter is not suitable for the present purpose. The use of a long filament often employed for this purpose is not appropriate to the flow method, since the pressure difference along the filament becomes too large at a high rate of reaction.

Two-filament Method. — In the present work, two filaments differing in length are used and the end effect of the longer filament is compensated with that of the shorter one. Two filaments, one longer (main) and the other shorter (compensating), of the same diameter and material are mounted in the vessel and heated one by one with the same current to obtain the reaction probabilities separately. Then, the reaction probability free from the end effect is obtained as follows. Let L_m and L_c denote the lengths of the two filaments ($L_m > L_c$) and k_m and k_c the respective reaction probabilities. Dividing the main filament into two end portions $L_c/2$ in length each and the middle portion $L_m - L_c$ in length, the reaction probability k_m can be expressed as a weighted mean of the probability k'_c at the end portions and k' at the middle portion. Then, k' is given by

$$k' = (k_m L_m - k'_c L_c)/(L_m - L_c) \qquad (8)^{**}$$

When the two filaments are heated with the same current, the end portions of the longer one will attain the same distribution of temperature as that along the compensating filament, and the middle portion at a uniform temperature provided that the filaments are long enough. Therefore, k'_c is equal to k_c if the reaction probability is independent of the pressure of water vapor, and is equal to k_c at the same partial pressure of water vapor as that under which k_m is obtained if the probability depends upon the pressure. Therefore, if k_c is obtained at various pressures P of water vapor and plotted against P, k'_c is obtained graphically, and hence k', the reaction probability free from the end losses, can be evaluated by Eq. 8. Although the two filaments are heated under the same initial pressure, the partial pressure while the respective filament is being heated is not the same, owing to the difference in the reacting areas of the filaments.

Experimental

Apparatus. — The apparatus was essentially the same as that of the previous paper. Only the changed points will be described below.

A reaction vessel was 7.0 cm. in diameter and 30 cm. in length. In it two tungsten filaments each 0.114 mm. in diameter and 128 mm. and 81 mm. long, respectively, were mounted perpendicular to the axis of the vessel at a distance of 5 cm. from each other. The distributions of

1) N. Sasaki and T. Hamamura, This Bulletin, **29**, 365 (1956).

2) L. B. Thomas and R. E. Brown, *J. Chem. Phys.*, **18**, 1367 (1950).

* The probability of reaction of water molecule with the filament for a single collision.

** Eqs., Figs. and Tables are numbered following consecutively those of the previous paper (Ref. 1).

temperature along the filaments were previously determined by the method of Langmuir and others[3]. The tungsten filaments used were taken from the same spool as that used in the previous experiments and pretreated in a similar manner. A Pirani gauge having a sensitivity of 1.42×10^{-5} mmHg for hydrogen was attached to the glass balloons in place of McLeod manometer M_3. The wall in front of the filaments was protected from the blue deposit of reaction product by a glass tube containing an iron rod which was hung in the vessel with a thin wire and shifted by a solenoid only when the temperature was measured by an optical pyrometer.

Procedure.—Procedures of evacuating the apparatus, degassing the filaments and introducing water vapor into the vessel have been described previously[1]. When the flow of water vapor became stationary, the main filament was heated and the temperature was measured with an optical pyrometer. As the reaction proceeded the pressure in the glass balloons increased gradually and this increase was measured with the Pirani gauge, every two minutes for sixteen minutes. The filament was then cooled and the balloons were evacuated. After this treatment, the compensating filament was heated with the same current and the pressure increase was measured similarly for the same time. The pressure increase gave the rate of reaction, and hence k_m[4] and k_c were evaluated by Eq. 7 and P by Eq. 6. Variations of k_m and k_c with P at a definite temperature were determined by a series of the experiments carried out by heating the filaments with a fixed current under various initial pressures of water vapor.

The temperature of the vessel remained at room temperature throughout the experiments, the effect of the heated filament being negligible at its highest temperature.

Results and Discussion

The experiments were carried out at temperatures from 1430 to 1940°K and initial pressures of water vapor from 12×10^{-5} to 125×10^{-5} mmHg. Values of k_m and k_c obtained were plotted against P in a log–log plot, respectively. Some of them are shown in Fig. 5.

From these plots, values of k_m and k'_c at a definite pressure were obtained, and the probability k' free from the end losses was evaluated by Eq. 8. Values of k_m, k'_c and k' at 60×10^{-5} mmHg pressure of water vapor thus obtained are given in Table II. Plots of $\log k'$ vs. $1/T\times10^3$ at 30×10^{-5} and 60×10^{-5} mmHg of water vapor are given in Fig. 6. Humps observed in the curves in the vicinity of 1700°K were not observed in the previous

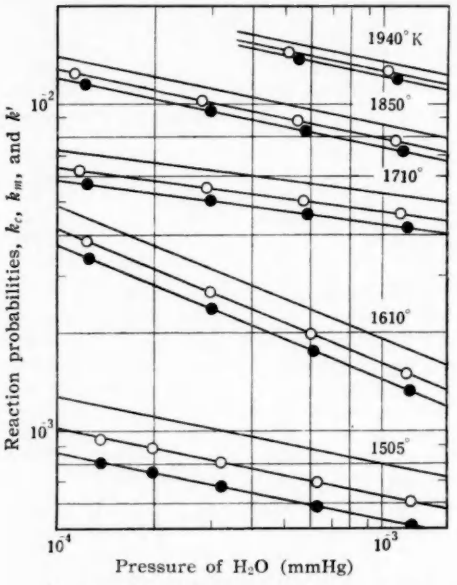

Fig. 5. Effect of pressure of water vapor on the reaction probabilities, k', k_m and k_c.
—— k', —○— k_m, —●— k_c

TABLE II. REACTION PROBABILITIES AT 60×10^{-5} mmHg PRESSURE OF WATER VAPOR

Temp. of filament (°K)	k_m	k_c	k'
1430	$3.3_4\times10^{-4}$	$2.6_3\times10^{-4}$	$4.5_7\times10^{-4}$
1470	$5.1_6\times10^{-4}$	$4.2_0\times10^{-4}$	$6.8_2\times10^{-4}$
1505	$7.0_2\times10^{-4}$	$5.9_1\times10^{-4}$	$8.8_4\times10^{-4}$
1560	$1.2_2\times10^{-3}$	$1.0_6\times10^{-3}$	$1.4_9\times10^{-3}$
1610	$1.9_8\times10^{-3}$	$1.7_6\times10^{-3}$	$2.3_4\times10^{-3}$
1675	$4.0_8\times10^{-3}$	$3.6_7\times10^{-3}$	$4.7_9\times10^{-3}$
1710	$4.9_8\times10^{-3}$	$4.5_7\times10^{-3}$	$5.7_0\times10^{-3}$
1760	$5.3_2\times10^{-3}$	$4.9_4\times10^{-3}$	$5.9_8\times10^{-3}$
1850	$8.7_3\times10^{-3}$	$8.2_5\times10^{-3}$	$9.5_6\times10^{-3}$
1940	$1.4_0\times10^{-2}$	$1.3_5\times10^{-2}$	$1.4_8\times10^{-2}$

experiments, perhaps because of insufficient points of observation. No hysteresis was observed in the whole range of temperatures. The apparent heat of activation at 60×10^{-5} mmHg of water vapor is plotted against the filament temperature in Fig. 7.

Plots of $\log k'$ vs. $\log P$ at various temperatures are also shown in Fig. 5. It is evident that the elimination of end losses is significant especially at lower temperatures. It was found from this figure that the reaction probability decreased with increase of the pressure of water vapor. Although this decrease seemed to be

3) I. Langmuir, S. MacLane and K. Blodgett, *Phys. Rev.*, **35**, 478 (1930).
4) The roughness factor of 1.225 was used according to Tonks. L. Tonks, *Phys. Rev.*, **38**, 1030 (1931).

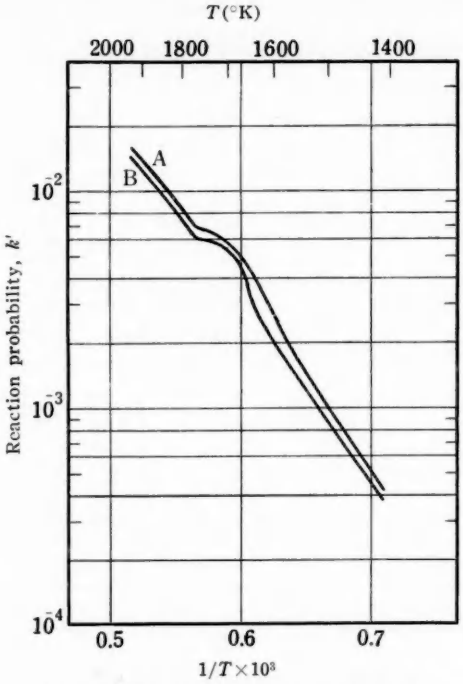

Fig. 6. Effect of filament temperature on the reaction probability k' at 30×10^{-5} and 60×10^{-5} mmHg of water vapor. A—30×10^{-5} mmHg, B—60×10^{-5} mmHg.

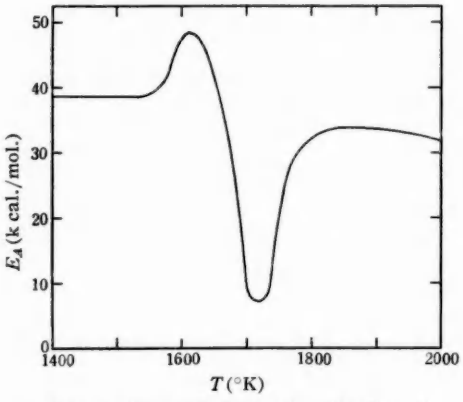

Fig. 7. Apparent heat of activation at 60×10^{-5} mmHg of water vapor.

caused by cooling of the filament by water vapor or by decrease of the reaction probability itself, the lowering of the temperature was not observed by either the optical pyrometer or the resistance of filament.

At filament-temperatures and pressures of water vapor plotted in Fig. 5, the reaction rates were independent of hydrogen pressures. Effect of hydrogen pressure on the reaction rate will be described in the following paper.

From the plot of $\log k'$ vs. $\log P$ the order n of reaction with respect to water vapor can be determined. As described in the previous paper, the rate of reaction D is given by

$$D=k'SBP \tag{5}$$

The reaction rate depends only upon the pressure of water vapor, when the filament temperature is fixed, as

$$D=KP^n \tag{9}$$

where K and n are constants. Eliminating D from Eqs. 5 and 9, k' is given by

$$k'=K/SB\times P^{n-1} \tag{10}$$

or

$$\log k'=\log(K/SB)+(n-1)\log P \tag{11}$$

The value of $n-1$ is thus given as the slope of the curve of $\log k'$ plotted against $\log P$ as in Fig. 5. The order of reaction thus obtained are tabulated in Table III. The reaction is nearly the first order.

TABLE III. ORDER OF REACTION

Temp. of filament (°K)	1505	1610	1710	1850	1940
Order of reaction, n	0.8_0	0.6_0	0.8_8	0.8_0	0.8_0

Summary

1) The end effect of filament upon the reaction probability was eliminated by means of the two-filament method. Its principle and procedure were described.

2) Reaction probabilities were determined at temperatures from 1430 to 1940°K and pressures of water vapor from 12×10^{-5} to 125×10^{-5} mmHg.

3) The reaction probability increased remarkably with the increase of temperature, but the rate of increase became smaller in the vicinity of 1700°K.

4) The order of reaction with respect to water vapor was found to lie between 0.6_0 and 0.8_6.

The author wishes to express sincere thanks to Professor N. Sasaki of Kyoto University and Professor K. Kodera of Kyoto Technical University for their kind discussion and encouragement.

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The Kinetic Study of Surface-chemical Reactions at Extremely Low Pressures. III. The Thermal Reaction between Water Vapor and a Tungsten Filament. Part III

By Takuya HAMAMURA

(Received March 17, 1959)

In continuation of the previous papers[1,2] in which the kinetics of the reaction of water vapor with tungsten was studied, this paper is concerned with the study of the effect of hydrogen pressure on the reaction rate, which seems to give some information about the adsorbed layer on the filaments surface.

Experimental

Apparatus. — The apparatus was essentially the same as that used in the previous experiments, except for an equipment for the control of hydrogen pressure. The pressure of hydrogen in the reaction vessel was changed by an adjustable needle valve placed in the path between trap 6 and diffusion pump 7 in Fig. 1*. If the flow of hydrogen in the path obeys Knudsen's law of molecular flow and the back diffusion through the pump is negligibly small, the quantity D in moles of hydrogen which flow into the balloons per second is given by the following equation similar to Eq. 1'

$$D = A'\overline{B}'P' \tag{12}$$

where A' is the over-all conductance of the path from the reaction vessel to the pump, $\overline{B}'$ is a constant determined experimentally, and P' is the partial pressure of hydrogen in the vessel. Therefore, when A' was changed by varying the conductance of the needle valve, P' was changed correspondingly. The above procedure, however, did not change the pressure of water vapor in the vessel, since the conductance A of the path from the vessel to trap 6 was not changed even if A' was changed. The value of $A'\overline{B}'$ could be determined experimentally by measuring D and P' while hydrogen was flowing through the path. Thus after knowing $A'\overline{B}'$, P' could be calculated from the measured value of D.

The needle valve is shown schematically in Fig. 8. When the mercury was lowered, hydrogen flowed mainly through the wide tube, and when the mercury was raised to cut the wide tube off, it flowed through the capillary with a smaller conductance, then by moving a glass needle containing an iron rod by a solenoid into the capillary, the conductance could be decreased further. The over-all conductance of the path from the reaction vessel to the diffusion pump was 4.90×10^{-3} cm^2 when the mercury was lowered, 1.21×10^{-3} cm^2 when the mercury was raised and the needle was drawn out of the capillary, and 3.15×10^{-4} cm^2 when the whole length of the needle was in the capillary.

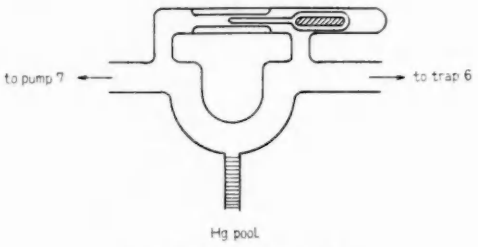

Fig. 8. The needle valve.

A tungsten filament 0.114 mm. in diameter and 81 mm. long was used. This was taken from the same spool as that used in the previous experiments and pretreated in a similar manner. A Pirani gauge of the same type as that attached to the glass balloons was attached to the reaction vessel.

Procedure.—The procedures of evacuating the apparatus, degassing the filament and introducing water vapor into the vessel were described previously. When the flow of water vapor became stationary, the pressure was measured with a quartz fiber manometer, and the filament was then heated to a desired temperature, the conductance of the needle valve being kept at a desired value. The pressure increase of the glass balloons was measured in a similar manner as mentioned previously. The pressure increase gave the reaction rate, and the hydrogen pressure in the vessel was calculated by Eq. 12. Thus, the effect of hydrogen pressure on the reaction rate was determined by the experiments carried out by heating the filament under various conductances of the valve at a fixed temperature and a constant initial pressure of water vapor. The temperature of the reaction vessel remained at room temperature throughout the experiments.

Results

The experiments were carried out at filament temperatures of 1850 and 1940°K

1) N. Sasaki and T. Hamamura, This Bulletin, **29**, 365 (1956).
2) T. Hamamura, ibid., **32**, 845 (1959).
* Eqs. and Figs. are numbered after those of the previous papers.

under 12×10^{-5} and 32×10^{-5} mmHg initial pressures of water vapor and at 1510, 1615, 1850 and 1940°K under 62.5×10^{-5} mmHg.

The reaction rate was independent of the hydrogen pressure below 1850°K at all the initial pressures of water vapor studied. At 1940°K, however, the reaction rate was independent of the hydrogen pressure at 62.5×10^{-5} mmHg of water vapor, but decreased with the increase of hydrogen pressure gradually at 32×10^{-5} mmHg and steeply at 12×10^{-5} mmHg. These are shown in Fig. 9. It was apparent from these results that the reaction rate was independent of the hydrogen pressure at lower filament temperatures or higher pressures of water vapor but decreased with the increase of hydrogen pressure at higher filament temperatures and lower pressures of water vapor. Moreover, the reaction rate decreased more steeply as the temperature increased or the pressure of water vapor decreased.

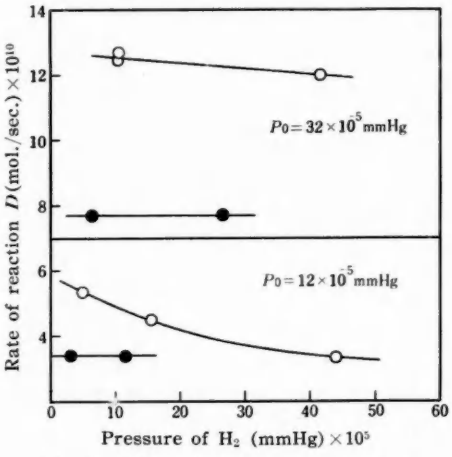

Fig. 9. Effect of hydrogen pressure on the reaction rate. ●-1850°K, ○-1940°K.

Discussion

The reaction rate might decrease owing to the retardation of the reaction by hydrogen or might decrease owing to the uptake of hydrogen by the wall, because the rate was calculated from the pressure increase of the glass balloons. The independency of reaction rates upon the hydrogen pressures at lower filament temperatures or higher pressures of water vapor might suggest that neither retardation nor uptake occurred under these conditions. As for the uptake, the following facts are known by the studies[3,4] of Langmuir: when a tungsten filament is heated above 1300°K in hydrogen at low pressure, the hydrogen gradually disappears. This action is caused by the hydrogen dissociated into atoms in contact with the filament, the atom then being driven on to the bulb and there held by adsorption. But the disappearance of hydrogen is suppressed almost completely by a trace of oxygen or water vapor at lower filament temperatures, presumably because of the formation of an adsorbed layer of oxygen acting as a catalytic poison against the dissociation of hydrogen. In the present work, too, the filament surface might be covered with oxygen at lower temperatures or higher pressures of water vapor, and in consequence neither retardation nor uptake occurred. However, the disappearance is known to take place again when the filament temperature rises or the pressure of oxygen or water vapor decreases, probably because of desorption of the adsorbed layer. In the present work, the reaction rate was found to decrease at higher temperatures and lower pressures of water vapor. This seemed to suggest that the decrease was caused by the uptake of hydrogen by the wall, the effect being known as "clean up".

Summary

Hydrogen hardly affected the reaction at lower filament temperatures or higher pressures of water vapor, but it decreased the rate of reaction at higher temperatures and lower pressures, as ascribed to the "clean up" of hydrogen by the filament.

The author wishes to express sincere thanks to Professor N. Sasaki of Kyoto University and Professor K. Kodera of Kyoto Technical University for their kind discussion and encouragement.

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3) I. Langmuir, *J. Am. Chem. Soc.*, **34**, 1310 (1912).
4) I. Langmuir, ibid., **38**, 2221 (1916).

The Infrared Spectra of Alkane-1-sulfonates

By Kuniaki FUJIMORI

(Received September 13, 1958)

Several investigations have been made on the characteristic infrared absorptions of sulfur-oxygen compounds such as sulfones or sulfone amides, and 1350~1300 cm^{-1} and 1160~1120 cm^{-1} bands were attributed to $-SO_2-$ group[1,2]. On sulfonic acids or their salt, however, there can not be found any systematic studies on their characteristic infrared absorptions. Bellamy[3] proposed 1200~1160 cm^{-1} and 1060~1030 cm^{-1} bands as the characteristic infrared absorptions of $-SO_3-$ group based on his results for aromatic sulfonates. Simon and Kriegsmann[4] investigated Raman and infrared spectra of alkali metal salts of methanesulfonic acid, and discussed these spectra under the assumption that methanesulfonate ion has the symmetry property of C_{3v}. Houlton and Tartar[5] investigated Raman spectra of several *n*-alkane-1-sulfonates in aqueous solution, compared these spectra with those of other sulfur compounds, and proposed some assignments.

Since the assignments so far given seem not to be decisive, the author studied infrared spectra of alkane-1-sulfonates where carbon numbers are 1—8 and 12 in the solid state. Taking into account the theoretical result given in the succeeding paper[6] and the spectra of CXY_3 type molecules, the spectra of methanesulfonate ion were assigned. Furthermore, the characteristic infrared absorptions of sulfonic group and C–S bond in the sulfonic acids were assigned for higher sulfonates.

Results and Discussion

The infrared spectra of sulfonates are shown in Figs. 1—9.

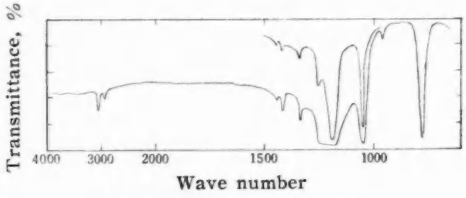

Fig. 1. Methanesulfonate.

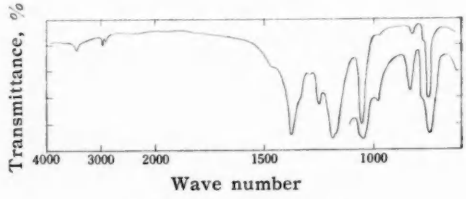

Fig. 2. Ethanesulfonate.

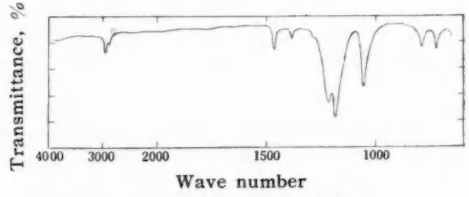

Fig. 3. *n*-Propane-1-sulfonate.

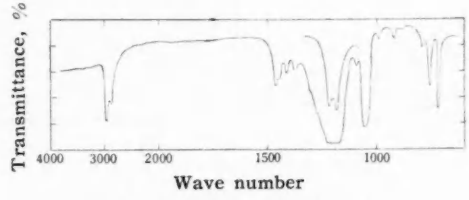

Fig. 4. *n*-Butane-1-sulfonate.

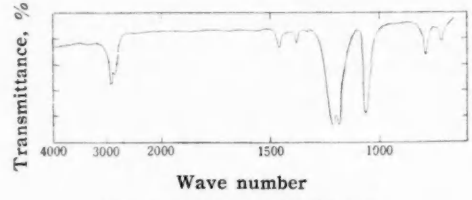

Fig. 5. *n*-Pentane-1-sulfonate.

1) K. C. Schreiber, *Anal. Chem.*, **21**, 1169 (1949).
2) L. J. Bellamy "The Infrared Spectra of Complex Molecules", Methuen & Co., Ltd., London, (1954), p. 297. And also see references cited there.
3) Idem., ibid., p. 301.
4) A. Simon and H. Kriegsmann, *Chem. Ber.*, **89**, 1718 (1956); *Z. physik. Chem.*, **209**, 369 (1955).
5) H. G. Houlton and A. V. Tartar, *J. Am. Chem. Soc.*, **60**, 544 (1938).
6) K. Fujimori, This Bulletin, **32**, 621 (1959).

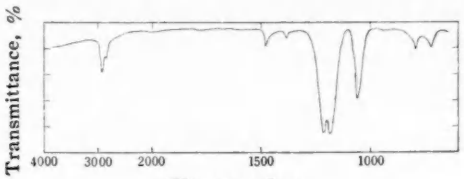

Fig. 6. *n*-Hexane-1-sulfonate.

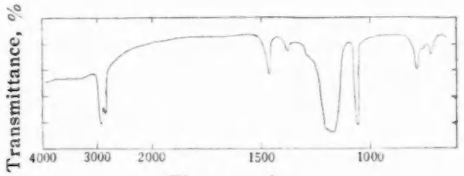

Fig. 7. *n*-Heptane-1-sulfonate.

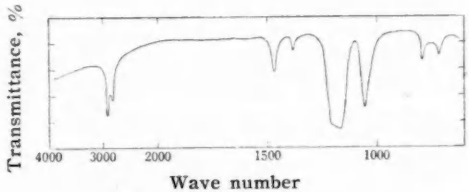

Fig. 8. *n*-Octane-1-sulfonate.

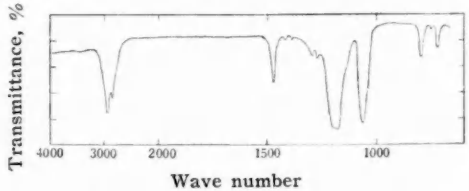

Fig. 9. *n*-Dodecane-1-sulfonate.

For lower homologues the C–H stretching frequencies have wave numbers higher than 2950 cm^{-1}. For higher homologues they decrease and gradually approach to those of hydrocarbons. This result is shown in Table I.

TABLE I. C–H STRETCHING VIBRATIONS (in cm^{-1})

N_C	Wave No.	Wave No.	N_C	Wave No.	Wave No.
1	3024 (w)	2944 (w)	6	2935 (s)	2850 (s)
2	2988 (w)	2944 (w)	7	2926 (s)	2855 (s)
3	2960 (m)	2880 (m)	8	2926 (s)	2855 (s)
4	2944 (s)	2880 (m)	12	2924 (s)	2855 (s)
5	2940 (s)	2870 (s)			

The C–H deformation vibrations are found at 1450~1470 cm^{-1} and at 1380 cm^{-1} and are summarized in Table II.

TABLE II. C–H DEFORMATION VIBRATIONS (in cm^{-1})

N_C	Wave No.	Wave No.	N_C	Wave No.	Wave No.
1	1436 (m)	1418 (m)	6	1462 (m)	1380 (w)
2	1450 (m)	1383 (m)	7	1467 (m)	1380 (w)
3	1461 (m)		8	1468 (m)	1380 (w)
4	1468 (m)	1378 (m)	12	1468 (m)	1380 (w)
5	1464 (m)	1379 (m)			

As to the assignments of S–O stretching and C–S stretching vibrations methanesulfonate ion was dealt with at first. In this case relatively stronger absorptions at 1192, 1060 and 789 cm^{-1} were found. As shown in the preceding paper[6], only three stretching vibrations, ν_1, ν_2 and ν_4, are expected to appear in the rock salt region, where ν_1 is S–CH_3 stretching, ν_2 S–O symmetric stretching, and ν_4 S–O degenerate stretching vibration. From the result of normal coordinate treatment and the comparison of similar molecules given in Table III, the assignments for the spectra of methanesulfonate ion are determined as shown in the table.

TABLE III. COMPARISON OF THE SPECTRA OF $(CH_3)SO_3^-$ AND SIMILAR MOLECULES (in cm^{-1})

Molecules	ν_1	ν_2	ν_4
CH_3D	2205	2982	3030
CH_3F	1050	2863	3009
CCl_3Br	418	710	765
$SO_3(CH_3)^-$	789	1060	1192

The weak absorption at 970 cm^{-1} may be attributed to the rocking vibration of the methyl radical. Simon and Kriegsmann[4] and Siebert[7] reached the same conclusion.

Comparing the absorptions of the higher sulfonates with those of methanesulfonate, the assignments can be made as listed in Tables IV—VI.

About C–S stretching vibration, Simon and Kriegsmann[4] and Siebert[7] reached almost the same conclusion for the cases of

TABLE IV. DOUBLY DEGENERATED AND DOUBLET VIBRATIONS OF S–O STRETCHING VIBRATIONS (in cm^{-1})

N_C	Wave No.	Wave No.	N_C	Wave No.	Wave No.
1		1192	6	1216	1180
2		1180	7		1175
3	1224	1182	8		1175
4	1200	1186	12		1175
5	1210	1184			

All absorptions are strong.

7) H. Siebert, *Z. anorg. u. allgem. Chem.*, **289**, 15 (1957).

TABLE V. SYMMETRIC S-O STRETCHING VIBRATION (in cm^{-1})

N_C	Wave No.	N_C	Wave No.
1	1060	6	1062
2	1056	7	1062
3	1055	8	1062
4	1053	12	1063
5	1060		

All absorptions are strong.

TABLE VI. C-S STRETCHING VIBRATION (in cm^{-1})

N_C	Wave No.	N_C	Wave No.
1	789 (s)	6	787 (m)
2	751 (m)	7	792 (m)
3	783 (m)	8	792 (m)
4	793 (m)	12	798 (m)
5	787 (m)		

TABLE VII. ROCKING VIBRATION OF $-(CH_2)_n-$ GROUP (in cm^{-1})

n	Wave No.	n	Wave No.
2	726 (w)	5	720 (w)
3	759 (m)	6	720 (w)
	723 (m)	7	720 (w)
4	720 (w)	11	721 (w)

methane- and ethane-sulfonates. However, the rocking vibration of $-(CH_2)_n-$ group in the n-alkyl radical is expected to be at about 750 cm^{-1} when n is 2 and at 730~720 cm^{-1} when n is greater than 3. Some irregularity found in Table VI may be due to the coupling of C-S stretching vibration with this CH_2 rocking vibration of $-(CH_2)_n-$ group is summarized in Table VII.

The absorptions at 1250 cm^{-1} of methane- and ethane-sulfonates, at 836 cm^{-1} of ethane-sulfonate may be attributed to overtones or combination tones.

Experimental

Samples. — *Methanesulfonate.* — Methanesulfonic acid (pure reagent grade) was distilled in vacuo (b. p. 160°C at 5 mmHg) and the aqueous solution was neutralized with sodium carbonate and evaporated to dryness. Sodium methanesulfonate was recrystallized from 90% ethanol.

Ethanesulfonate.—Ethyl mercaptane (b. p. 37°C) was oxidized with concentrated nitric acid[8] and the reaction mixture was neutralized with sodium carbonate (10% aqueous solution), the sulfonate solution was evaporated to dryness and extracted with hot ethanol to separate inorganic salts. The sulfonate was recrystallized from ethanol.

Other sulfonates.—Sulfonates other than above described were prepared by Strecker reaction[9]. Corresponding chloride was heated from 180 upto 200°C in a stainless steel autoclave for 10~16 hr. with sodium sulfite (anhydride) and water. The reaction mixture was filtered and evaporated to dryness. The residue was washed with petroleum ether (b. p. 30~40°C) and the sulfonate was extracted with hot ethanol and recrystallized from ethanol.

Absorption Measurement. — The infrared spectra were obtained with a Perkin-Elmer Model 21 double beam infrared spectrophotometer using NaCl prism. The KBr disk method was employed to obtain the spectra in solid state.

The author expresses his indebtedness to Dr. A Kotera, Professor of Tokyo University of Education, and Dr. T. Shimanouchi, Assistant Professor of the University of Tokyo, under whose kind direction this work was performed. He also thanks Mr. Y. Ikegami, Fellow of Tohoku University, for his cooperation to obtain infrared spectra and Mr. Y. Akai, Chief of Research Section of Funakawa Refinery, for his encouragement of this research.

Nippon Mining Co., Funakawa Refinery
Oga-shi, Akita

8) D. L. Vivian and E. E. Reid, *J. Am. Chem. Soc.*, **57**, 2559 (1935).
9) R. M. Reed and H. V. Tartar, ibib., **57**, 571 (1935).

LCAO SCF Calculation on Anthracene and Reactivity Indexes in SCF Method

By Kenichi FUKUI, Keiji MOROKUMA and Teijiro YONEZAWA

(Received January 30, 1959)

In order to interpret chemical reactivity of conjugated molecules, there have been proposed several quantum-mechanical methods in LCAO MO treatment, such as the frontier electron method (frontier electron density and superdelocalizability as reactivity indexes[1]), the static method (total π-electron density and self-polarizability for an ionic reaction and free valence for a radical reaction)[2], the localization method (localization energy)[3], and so on.

Within the scope of the simple LCAO MO treatment, where electronic interaction is not explicitly considered, total π-electron density of an alternant hydrocarbon is unity for all the positions[4], and accordingly in terms of the static method the ionic reactivity is to be determined by self-polarizability of each position. But once electronic interaction is taken into account, the uniformity of total π-electron distribution is immediately extinguished, so that its magnitude comes to correspond to the ionic reactivity in a molecule in the static method. For *trans*-butadiene the coefficients of AO's in MO's, calculated in semi-empirical SCF method[5], in non-empirical SCF method[6] and in non-empirical SCF CI method[7], show the larger π-electron density, i. e., the larger electrophilic reactivity, at the position 2, contradictory to the experiments. Further, semi-empirical SCF calculation on naphthalene leads to an erroneous prediction of electrophilic reactivity[8].

For the purpose of obtaining more information on reactivity indexes, in the first two paragraphs of the present paper, we determine the coefficients of AO's in MO's of anthracene by semi-empirical LCAO SCF method and discuss on some physico-chemical properties. In the last paragraph it is examined whether or not each of total π-electron density, free valence and frontier electron density remains a good index of chemical reactivity in SCF treatment.

Method

Roothaan has developed in detail the general formalism of LCAO SCF method for the closed configuration of a molecule[9]. This will not be repeated here for the sake of brevity. Using his theory with only π-electrons considered explicitly, we numerically calculate the coefficients of AO's in SCF MO's of the ground state of anthracene.

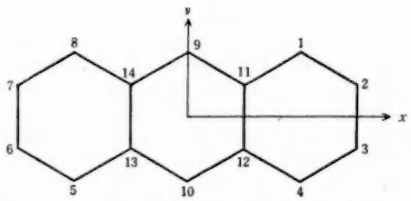

Fig. 1. The numbering of atoms and the coordinate of symmetry operation of anthracene.

The numbering of atoms and the coordinate of symmetry operation are shown in Fig. 1. The bond distances are taken to be 1.370 Å for the bond 1—2, 1.396 Å for 9—11, 1.408 Å for 2—3, 1.423 Å for 1—11 and 1.436 Å for 11—12, and all the bond angles are assumed in a good approximation to be 120°[10].

Necessary numerical evaluation of the reasonance integral, $\beta_{\mu\nu}$, and the coulomb repulsion integral, $\gamma_{\mu\nu}$, are carried out on the semi-empirical formulae proposed by

1) K. Fukui et al., *J. Chem. Phys.*, **20**, 722 (1952); **22**, 1433 (1954); This Bulletin, **27**, 423 (1954).
2) C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc. (London)*, **A191**, 39 (1947); **A192**, 16 (1947); F. H. Burkitt et al., *Trans. Faraday Soc.*, **47**, 553 (1951).
3) G. W. Wheland, *J. Am. Chem. Soc.*, **64**, 900 (1940).
4) C. A. Coulson and S. Rushbrooke, *Proc. Cambridge Phil. Soc.*, **36**, 193 (1940).
5) C. M. Moser, *Compt. rend.*, **238**, 1585 (1954).
6) R. G. Parr and R. S. Mulliken, *J. Chem. Phys.* **18**, 1338 (1950).
7) A. Pullman and J. Baudet, *Compt. rend.*, **238**, 241 (1954); A. Pullman *J. chim. phys.*, **51**, 188 (1954).
8) C. M. Moser, ibid., **52**, 24 (1955).
9) C. C. J. Roothaan, *Revs. Mod. Phys.*, **23**, 69 (1951).
10) A. McL. Mathieson et al., *Acta Cryst.*, **3**, 245 (1950); V. C. Sinclair et al., ibid., **3**, 251 (1950). Deviations of all the observed bond angles from 120° are about 1~2°.

TABLE I. SCF MO'S AND THEIR ORBITAL ENERGIES OF ANTHRACENE

Symmetry	Orbital energy[a]	MO	
b_{1u}	$\varepsilon_1 = -5.762$	$\phi_1 = 0.4887\sigma_4 + 0.4448\sigma_5 + 0.3323\sigma_6 + 0.6730\sigma_7$	occupied
b_{2g}	$\varepsilon_2 = -5.190$	$\phi_2 = 0.5818\sigma_8 + 0.6276\sigma_9 + 0.5174\sigma_{10}$	
b_{1u}	$\varepsilon_3 = -3.350$	$\phi_3 = 0.3108\sigma_4 + 0.7098\sigma_5 - 0.3717\sigma_6 - 0.5113\sigma_7$	
b_{3g}	$\varepsilon_4 = -3.196$	$\phi_4 = 0.6278\sigma_{11} + 0.3465\sigma_{12} + 0.4423\sigma_{13} + 0.5386\sigma_{14}$	
a_{1u}	$\varepsilon_5 = -2.433$	$\phi_5 = 0.7932\sigma_1 + 0.4861\sigma_2 + 0.3668\sigma_3$	
b_{2g}	$\varepsilon_6 = -1.9935$	$\phi_6 = 0.0792\sigma_8 + 0.5894\sigma_9 - 0.8039\sigma_{10}$	
b_{3g}	$\varepsilon_7 = -0.2930$	$\phi_7 = 0.5130\sigma_{11} + 0.4221\sigma_{12} - 0.6793\sigma_{13} - 0.3117\sigma_{14}$	
b_{1u}	$\varepsilon_8 = +7.1389$	$\phi_8 = 0.4431\sigma_4 - 0.3746\sigma_5 - 0.7573\sigma_6 + 0.2997\sigma_7$	unoccupied
a_{1u}	$\varepsilon_9 = +7.6451$	$\phi_9 = 0.0811\sigma_1 + 0.5125\sigma_2 - 0.8548\sigma_3$	
b_{2g}	$\varepsilon_{10} = +9.124$	$\phi_{10} = 0.8095\sigma_8 - 0.5087\sigma_9 - 0.2932\sigma_{10}$	
b_{1u}	$\varepsilon_{11} = +9.668$	$\phi_{11} = 0.6843\sigma_4 - 0.3974\sigma_5 + 0.4219\sigma_6 - 0.4425\sigma_7$	
b_{3g}	$\varepsilon_{12} = +9.726$	$\phi_{12} = 0.1781\sigma_{11} - 0.5967\sigma_{12} - 0.5090\sigma_{13} + 0.5943\sigma_{14}$	
a_{1u}	$\varepsilon_{13} = +11.747$	$\phi_{13} = 0.6035\sigma_1 - 0.7079\sigma_2 - 0.3671\sigma_3$	
b_{3g}	$\varepsilon_{14} = +12.069$	$\phi_{14} = 0.5576\sigma_{11} - 0.5880\sigma_{12} + 0.2895\sigma_{13} - 0.5095\sigma_{14}$,	

where[b]

$\sigma_1 = (1/2)(\phi_1 - \phi_4 + \phi_5 - \phi_8)$, $\sigma_2 = (1/2)(\phi_2 - \phi_3 + \phi_6 - \phi_7)$, $\sigma_3 = (1/2)(\phi_{11} - \phi_{12} + \phi_{13} - \phi_{14})$,
$\sigma_4 = (1/2)(\phi_1 + \phi_4 + \phi_5 + \phi_8)$, $\sigma_5 = (1/2)(\phi_2 + \phi_3 + \phi_6 + \phi_7)$, $\sigma_6 = (1/\sqrt{2})(\phi_9 + \phi_{10})$,
$\sigma_7 = (1/2)(\phi_{11} + \phi_{12} + \phi_{13} + \phi_{14})$, $\sigma_8 = (1/2)(\phi_1 + \phi_4 - \phi_5 - \phi_8)$, $\sigma_9 = (1/2)(\phi_2 + \phi_3 - \phi_6 - \phi_7)$,
$\sigma_{10} = (1/2)(\phi_{11} + \phi_{12} - \phi_{13} - \phi_{14})$, $\sigma_{11} = (1/2)(\phi_1 - \phi_4 - \phi_5 + \phi_8)$, $\sigma_{12} = (1/2)(\phi_2 - \phi_3 - \phi_6 + \phi_7)$,
$\sigma_{13} = (1/\sqrt{2})(\phi_9 - \phi_{10})$, $\sigma_{14} = (1/2)(\phi_{11} - \phi_{12} - \phi_{13} + \phi_{14})$

a) W_{2p} as standard. In units of eV.

b) ϕ_i is the AO on the i-th atom.

Pariser and Parr[11]. In the expression of the coulomb integral, α_μ,

$$\alpha_\mu = W_{2p} - \sum_{\nu(\neq\mu)} \{\gamma_{\mu\nu} + (\nu : \mu\mu)\} \qquad (1)$$

no particular values of the coulomb penetration integral, $(\nu : \mu\mu)$, have been given by Pariser and Parr, and on the theoretical consideration[12] we have determined its average value as 0.85 eV. when the atoms μ and ν are adjacent, as 0.08 eV. when μ and ν are separated by a single atom, and as zero otherwise. W_{2p} in Eq. 1 is as usual the electronic energy of a carbon atom in its valence state and is regarded as a constant.

Results and Discussion on Anthracene

The obtained SCF MO's, ϕ_i, of the ground state of anthracene and their orbital energies, ε_i, are collected in Table I, together with non-occupied MO's.

Ionization Potential. — Putting $W_{2p} = -11.28$ eV.[11], we obtain 11.57 eV. as the first ionization potential of anthracene, which is, though no experimental results are available, much larger than the estimated value, 7.23 eV., by Matsen[13]. Giving too large calculated value is not particular to the case of anthracene, but the general tendency of SCF calculation[5,6,8]; on this point a discussion shall be made in near future.

Electronic Spectra. — The energies of configurations, the values of interconfigurational matrix elements and wave functions of the excited states are listed in

TABLE II. THE ENERGIES OF CONFIGURATIONS, THE VALUES OF INTERCONFIGURATIONAL MATRIX ELEMENTS AND THE EXCITED STATES WAVE FUNCTIONS[a]

B_{2u}: $[66 \mid 99] = 5.535$, $[69 \mid 96] = 0.551$,
$[77 \mid 88] = 5.419$, $[78 \mid 87] = 0.885$.
$E(V_{78}) - E_0 = 3.782$, $E(V_{69}) - E_0 = 5.206$,
$E(T_{78}) - E_0 = 2.013$, $E(T_{69}) - E_0 = 4.104$.
$[67 \mid 89] = -0.094$, $[69 \mid 87] = 0.369$.
$\langle V_{78} \mid V_{69} \rangle = 0.833$, $\langle T_{78} \mid T_{69} \rangle = 0.094$.
$\Psi(^1B_{2u}^-) = 0.908\ V_{78} - 0.418\ V_{69}$,
$\Psi(^1B_{2u}^+) = 0.418\ V_{78} + 0.908\ V_{69}$,
$\Psi(^3B_{2u}^-) = 0.999\ T_{78} - 0.045\ T_{69}$,
$\Psi(^3B_{2u}^+) = 0.045\ T_{78} + 0.999\ T_{69}$.

B_{3u}: $[66 \mid 88] = 5.145$, $[68 \mid 86] = 0.348$,
$[77 \mid 99] = 5.198$, $[79 \mid 97] = 0.502$.
$E(V_{79}) - E_0 = 3.743$, $E(V_{68}) - E_0 = 4.684$,
$E(T_{79}) - E_0 = 2.740$, $E(T_{68}) - E_0 = 3.987$.
$[76 \mid 89] = -0.094$, $[79 \mid 86] = -0.415$.
$\langle V_{79} \mid V_{68} \rangle = -0.736$, $\langle T_{79} \mid T_{68} \rangle = 0.094$
$\Psi(^1B_{3u}^+) = 0.877\ V_{79} + 0.480\ V_{68}$,
$\Psi(^1B_{3u}^-) = 0.480\ V_{79} - 0.877\ V_{68}$,
$\Psi(^3B_{3u}^-) = 0.997\ T_{79} - 0.075\ T_{68}$,
$\Psi(^3B_{3u}^+) = 0.075\ T_{79} + 0.997\ T_{68}$.

a) In units of eV.

11) P. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 465, 767 (1953).
12) R. G. Parr and B. L. Crawford, ibid., **16**, 1049 (1948).
13) F. A. Matsen, ibid., **24**, 602 (1956).

TABLE III. THE EXCITATION ENERGIES AND THE OSCILLATOR STRENGTHS OF ANTHRACENE

Symmetry	Excitation energy (eV.)		Oscillator strength	
	Calcd.	Obsd.	Calcd.	Obsd.
$^1B_{2u}^-$	3.40	3.30[a]	0.15	~0.1[a]
$^1B_{3u}^+$	3.34	3.50[a]	0.20	~0[a]
$^1B_{3u}^-$	5.09	4.80[a]	1.94	2.20[a]
$^1B_{2u}^+$	5.59	5.64[a]	1.01	0.65[a]
$^3B_{2u}^-$	2.01	1.8[b]	0.00	—
$^3B_{3u}^-$	2.73	—	0.00	—
$^3B_{3u}^+$	3.99	—	0.00	—
$^3B_{2u}^+$	4.11	—	0.00	—

a) H. B. Klevens and J. R. Platt, *J. Chem. Phys.*, **17**, 470 (1949).
b) G. N. Lewis and M. Kasha, *J. Am. Chem. Soc.*, **66**, 2100 (1944); S. P. McGlynn, M. R. Padhye and M. Kasha, *J. Chem. Phys.*, **23**, 593 (1955).

Table II, where only four lower excitations are considered. The calculated excitation energies and oscillator strengths are given in Table III, together with the observed values. The agreement with experiments is good, but for the inversion of excitation energies of $^1B_{2u}^-$ band and $^1B_{3u}^+$ band, which will be improved by the inclusion of more possible configurations.

Bond Order and Bond Distance. — Our SCF bond orders and observed bond distances are collected in Table IV, in comparison with the SCF bond orders by Pritchard and Sumner in a rough approximation[14] and with the bond orders in simple LCAO treatment. It is seen in Table IV that SCF bond orders in the present calculation are parallel with the observed bond distances except for the bond 11—12, in accordance with Pritchard and Sumner's result. The discrepancy in the bond 11—12 seems to indicate that the bond order of a bonding is not determined only by its length but by its nature; namely, whether the ending carbons of this bonding are primary, secondary or tertiary.

TABLE IV. THE BOND ORDERS AND OBSERVED BOND DISTANCES OF ANTHRACENE

Bond	Bond order			Obsd. bond distances (Å)[b]
	Present treatment	Pritchard and Sumner[a]	Simple LCAO	
1—2	0.8347	0.8422	0.7374	1.370
9—11	0.6107	0.6318	0.6061	1.396
2—3	0.4542	0.4493	0.5859	1.408
1—11	0.4383	0.4178	0.5354	1.423
11—12	0.5533	0.5484	0.4849	1.436

a) Ref. 14.
b) Ref. 10.

SCF Reactivity Indexes

First of all we define SCF frontier electron density in the same way as in simple LCAO treatment[1], where the frontier orbital denotes the highest occupied one for an electrophilic reaction, the lowest unoccupied one for a nucleophilic reaction, and both for a radical reaction.

The calculated results of total π-electron density, free valence and frontier electron densities of anthracene are given in Table V. Values of these reactivity indexes in SCF method of naphthalene and *trans*-butadiene are collected in Tables VI and VII, respectively.

Total π-electron density of anthracene is the largest at the position 11 and decreases in the order of 2, 1 and 9. The position 11 being out of the question because of its lack of hydrogen to be substituted, an electrophilic substitution should take place at the position 2 and a nucleophilic substitution at the position 9 on the basis of the static method. This prediction contradicts experimental results that the position 9 is the most reactive in an electrophilic substitution. Concerning naphthalene the position 2, where SCF total π-electron density has the largest value as shown in Table VI, does not actually suffer from an electrophilic substitution. Furthermore, as for butadiene Table VII shows that total π-electron densities by semi-empirical SCF method, by non-empirical SCF method and by non-empirical SCF CI method lead to the same erroneous prediction that the position 2 is the most susceptible to an electrophilic reaction. Thus SCF total π-electron density is no longer a good index for chemical reactivity.

On the contrary, it will be valuable to emphasize that SCF frontier electron density correctly predicts the most reactive positions, that is, the position 9 in anthracene, 1 in naphthalene and 1 in

14) H. O. Pritchard and F. H. Sumner, *Proc. Roy. Soc.*, **A226**, 128 (1954); H. O. Pritchard, private communication. Their assumptions are the same as those that are presented by Pople[15], the main points of which are (1) neglect of the coulomb penetration integral, and (2) assumption of equi-bond-length and of regular hexagone of carbon ring, and (3) that the coulomb repulsion integral, $\gamma_{\mu\nu}$, is expressed in the following form.
$\gamma_{\mu\nu}=e^2/R_{\mu\nu}$ ($R_{\mu\nu}$: distance between the atoms μ and ν)
15) J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953).

TABLE V. VALUES OF SCF REACTIVITY INDEXES OF ANTHRACENE

Position	Total π-electron density	Free valence	Frontier electron density		
			Electrophilic	Nucleophilic	Radical
1	0.983	0.459	0.132	0.098	0.115
2	0.989	0.443	0.089	0.070	0.080
9	0.906	0.511	0.461	0.574	0.517
11	1.075	0.130	0.049	0.045	0.047

TABLE VI. VALUES OF SCF REACTIVITY INDEXES OF NAPHTHALENE[a)]

Position	Total π-electron density	Free valence	Frontier electron density		
			Electrophilic	Nucleophilic	Radical
1	0.967	0.453	0.334	0.339	0.343
2	1.003	0.435	0.166	0.162	0.157
9	1.062	0.158	0	0	0

a) Ref. 8.

TABLE VII. VALUES OF SCF REACTIVITY INDEXES OF *trans*-BUTADIENE

Position	Total π-electron density	Free valence	Frontier electron density		
			Electrophilic	Nucleophilic	Radical
A) Semi-empirical SCF method[a)]					
1	0.938	0.757	0.575	0.606	0.637
2	1.062	0.545	0.425	0.394	0.363
B) Non-empirical SCF method[b)]					
1	0.975	—	0.620	0.633	0.645
2	1.025	—	0.380	0.367	0.355
C) Non-empirical SCF CI method[c)]					
1	0.978	—	—	—	—
2	1.022	—	—	—	—

a) Ref. 5. b) Ref. 6. c) Ref. 7.

TABLE VIII. VALUES OF SCF FREE VALENCE OF HYDROCARBONS IN ROUGHER APPROXIMATION[a)]

Molecule	Position	Free valence
Naphthalene	1	0.447
	2	0.420
Anthracene	1	0.473
	2	0.441
	9	0.468
Phenanthrene	1	0.431
	2	0.408
	3	0.409
	4	0.428
	9	0.474
Chrysene	1	0.461
	2	0.464
	3	0.439
	4	0.434
	5	0.435
	6	0.436
Pyrene	1	0.432
	2	0.395
	4	0.485

a) Ref. 14.

butadiene for all the three kinds of reactions. It may be, therefore, concluded that frontier electron density remains a good reactivity index even when the electronic interaction is explicitly included.

So far as our approximation is concerned, free valence seems to give correct results in the three hydrocarbons, as shown in Tables V, VI and VII. In comparison with this, we have collected in Table VIII values of free valence of some hydrocarbons, which have been derived from the SCF bond orders obtained by Pritchard and Sumner[14]. It can be seen in Table VIII that this free valence leads to a seriously erroneous conclusion for anthracene and for pyrene: anthracene is, as is well known, the most susceptible to a radical attack at the position 9, and pyrene is so at 1. On inspection of these and other results of SCF calculation[16], it

16) G. Berthier, *J. chim. phys.*, **50**, 344 (1953); I. Tanaka, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **75**, 218 (1954); H. O. Pritchard and F. H. Sumner, *Trans. Faraday Soc.*, **51**, 457 (1955); etc.

may be said that the value of bond order, or that of free valence, varies very easily depending on the degree or approximation employed and on the semi-empirical method of evaluating atomic integrals. Such an unstable quantity would probably not deserve a reliable reactivity index.

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*Interaction entre les colorants et les surfactifs. II**

Par Tamotsu KONDO, Kenjiro MEGURO et Hidero NITO

(Reçu le 11 février 1959)

Dans le rapport précédent[1], les phénomènes de floculation et de défloculation de la rhodamine et de l'éosine en présence de surfactifs ont été systématiquement étudiés, et les mécanismes de ces phénomènes ont été proposés.

Nous allons essayer, dans le présent travail, d'élucider l'influence de la structure chimique de divers colorants sur les phénomènes de floculation et de défloculation.

Expériences

Matériels. — Les colorants que nous avons utilisés sont classifiés dans le Tableau I.

TABLEAU I. COLORANTS UTILISÉS

Classification	Valence	Nom
Colorants acides	−1	Orange de méthyle
	−1	Orange II
	−1	Na de sulfonate de *p*-hydroxyazobenzène
	−2	Orange G
	−2	Ponceau R
	−2	Tartrazine
Colorants basiques	+1	Jaune d'acridine
	+1	Bleu de méthylène
	+1	Violet de méthyle
	+1	Vert de méthyle
Colorants directs	−2	Benzopurpurine 4B
	−2	Rouge de congo
	−2	Chrysophénine G

Les surfactifs employés sont le bromure de dodécyl-pyridonium et le sodium de dodécyl-sulfate (que nous appellerons B.D.P. et S.D.S.). Leurs préparation et purification ont été déjà décrites dans un autre article[2].

Méthodes expérimentales.—Les méthodes adptées pour observer les phénomènes de floculation et de défloculation des colorants sont les mêmes que nous avons écrites précédemment[1].

Résultats

Floculation et défloculation des colorants par le B.D.P.—L'addition d'un peu de B.D.P. aux solutions de colorants acides a généralement causé la floculation des colorants. Dans le cas de la tartrazine, cependant, on n'a pas observé la floculation, mais on a trouvé seulement l'apparition de la turbidité.

Les floculés colorés ainsi formés étaient solubles dans le chloroforme qui ne dissout pas les colorants acides employés dans ce travail. On a pu extraire un corps coloré dans le chloroforme du mélange de tartrazine et de B.D.P. en solution. On doit alors penser que les floculés et le corps coloré sont des complexes formés entre les colorants et le B.D.P.

On a vu que les floculés ont été remis en solution en présence d'une quantité supérieure de B.D.P. Les concentrations de B.D.P. auxquelles les floculés commencent à défloculer étaient indépendantes de la C.C.M. (concentration critique micellaire) de cet agent cationique.

La valeur de floculation et celle de défloculation du B.D.P. étaient définies comme le minimum des concentrations nécessaires de cet agent pour floculer le colorant, et pour défloculer complètement le floculé[1], respectivement. Celle-là

* Une partie de ce rapport a été présentée à la réunion de chimie colloïdale de la société chimique du Japon qui s'est tenue à Kanazawa, au mois d'octobre 1957.

1) T. Kondo et K. Meguro, Ce Bulletin, **32**, 267 (1959).

2) O. Yoda, K. Meguro, T. Kondo et T. Ino, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **75**, 1272 (1954).

était presque indépendante de la structure chimique du colorant et celle-ci ne l'était pas. La différence de ces deux valeurs, que nous appellerons désormais la largeur de la zone de floculation, s'est accrue lorsqu'on a augmenté la concentration de colorant en solution. La Fig. 1 représente la relation entre la largeur de la zone de floculation et la concentration de colorant.

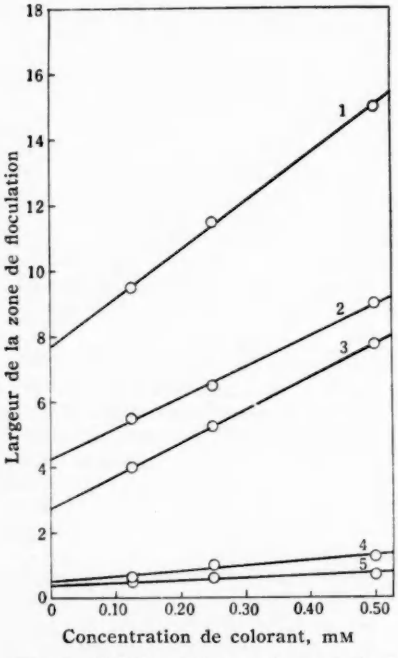


Fig. 1. Relation entre la largeur de la zone de floculation et la concentration de colorant. (1).

TABLEAU II. VALEURS DU N_d DU B.D.P.

Colorant	N_d
Orange de méthyle	14.8
Orange II	9.6
Na de sulfonate de *p*-hydroxyazobenzène	1.6
Orange G	10.2
Ponceau R	0.5

Le talus des lignes droites est caractéristique de chaque colorant et donne le nombre minimum des ions de surfactif qui est nécessaire pour disperser une molécule de complexe. Ce nombre a été nommé le nombre de défloculation, N_d, du surfactif[1]. Les valeurs obtenues sont données dans le Tableau II.

Floculation et défloculation des colorants basiques par le S.D.S.—La floculation du jaune d'acridine et du bleu de méthylène s'est effectuée par le S.D.S., tandis que celle du violet de méthyle et du vert de méthyle n'a jamais lieu par cet agent.

La formation d'un complexe coloré a été vérifiée par l'essai d'extraction dans le chloroforme ou l'acetate d'éthyle pour chaque cas de ces colorants. On a observé la défloculation du floculé en présence d'une quantité supérieure de S.D.S. La Fig. 2 fournit le diagramme qui indique la relation de la largeur de la zone de floculation avec la concentration de colorant.

On obtient la valeur du N_d du S.D.S. qui est de 9.8 et 8.1 pour le jaune d'acridine et le bleu de méthylène, respectivement, en utilisant le talus des lignes droites dans la Fig. 2.

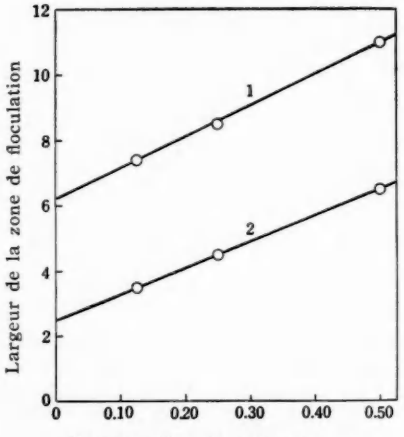


Fig. 2. Relation entre la largeur de la zone de floculation et la concentration de colorant. (2).

Floculation et défloculation des colorants directs.—Tous les colorants directs utilisés ont été floculés par un peu de B.D.P. Les concentrations de B.D.P. qui sont nécessaires pour la floculation des colorants étaient presque égales. Malgré l'addition d'une grande quantité de B.D.P., la défloculation de la benzopurpurine 4B n'a jamais été observée. Dans le cas du rouge de congo, le floculé a dispersé d'abord et ensuite refloculé, lorsque la concentration en agent cationique croît graduellement. On a trouvé pour la chrysophénine G que la zone de floculation et celle de défloculation ont paru deux fois alternativement quand on a graduellement

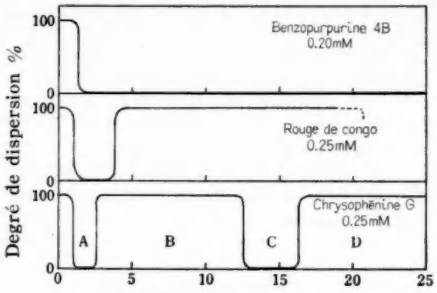


Fig. 3. Schéma de floculation des colorants directs.
A, Première zone de floculation;
B, Première zone de défloculation;
C, Deuxième zone de floculation;
D, Deuxième zone de défloculation.

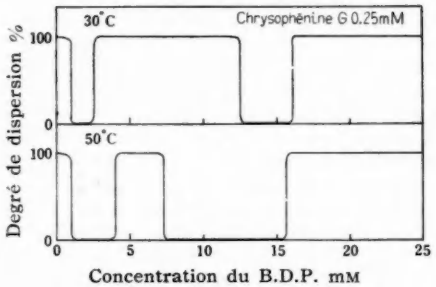


Fig. 4. Influence de la température sur la floculation de la chrysophénine G.

augmenté la de quantité B.D.P. en solution. Lorsqu'on a centrifugé les solutions de la première zone de défloculation, on a constaté qu'il y a eu la précipitation d'un corps coloré. La Fig. 3 donne le schéma de floculation de ces colorants directs.

L'élevation de la température a été accompagnée par la contraction de la première zone de défloculation de la chrysophénine G. Cela est indiqué dans la Fig. 4.

Considérations

Nous avons conclu précédemment[1] que la défloculation d'un complexe est due à la combinaison d'un certain nombre des ions de surfactif avec ce complexe et que le N_d n'y est pas nécessirement égal. A ce point de vue, nous allons examiner les résultats expérimentaux de la défloculation, car la floculation ne dépend pas rigoureusement de la structure chimique des colorants.

L'influence de la structure chimique du colorant sur le N_d.—Comparons d'abord les valeurs du N_d des colorants acides monovalents l'une à l'autre. Ces valeurs sont de 14.8, 9.6 et 1.6 pour l'orange de méthyle, l'orange II et le sodium de sulfonate de *p*-hydroxyazobenzène respectivement. Ces trois colorants ne diffèrent dans leur structure chimique que par le groupe nonionique lié au radical azoïque, comme le montre la Fig. 5.

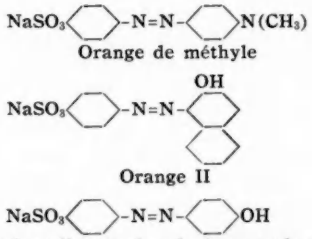


Fig. 5. Structures chimiques des colorants acides.

On doit, par suite, attribuer la différence de la valeur du N_d à celle de la structure du groupe nonionique du colorant.

Les affinités du phénol, du naphthol β et de la diméthylaniline pour l'eau diminuent dans l'ordre suivant:

Phénol > naphthol β > diméthylaniline.

On pourra conclure, en conséquence, que la valeur du N_d dépend profondément de l'affinité du groupe nonionique du colorant pour l'eau. C'est-à-dire, plus grande est l'affinité du groupe nonionique pour l'eau, plus petite est la valeur du N_d. L'ordre des valeurs du N_d pour ces colorants acides est en accord avec celui de leurs solubilités dans l'eau. En ce qui concerne des colorants acides bivalents, on peut aussi constater qu'un petit N_d de colorant amène une grande solubilité dans l'eau. La valeur du N_d du ponceau R, par exemple, est moins grande que celle de l'orange G qui est moins soluble que celui-là.

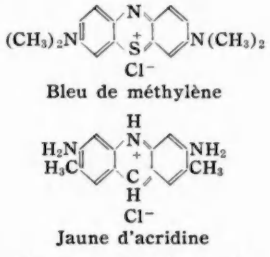
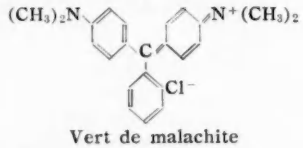


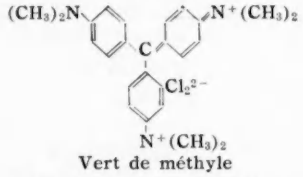
Fig. 6. Structures chimiques des colorants basiques (1).

Le jaune d'acridine et le bleu de méthylène ont les structures chimiques semblables l'une à l'autre comme les montre la Fig. 6. Le fait que les valeurs du N_d pour ces deux colorants sont presque égales sera du à la similarité des structures chimiques de ces colorants.

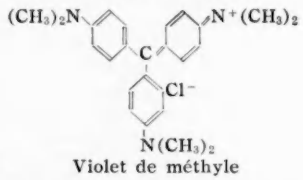
Floculation et défloculation des colorants de triphénylméthane.—On a déjà décrit que le violet de méthyle et le vert de méthyle, colorants de triphénylméthane, ne sont pas floculés par le S.D.S. La comparaison des résultats expérimentaux concernant le vert de malachite, qui est floculé et défloculé par le S.D.S.[3], à ceux du violet de méthyle et du vert de méthyle nous amène à examiner de l'influence de la structure chimique de ces colorants sur leur comportement dans les solutions du S.D.S. La Fig. 7 fournit les structures chimiques de ces trois colorants.



Vert de malachite



Vert de méthyle



Violet de méthyle

Fig. 7. Structures chimiques des colorants basiques (2).

Notons, par exemple, la différence de la structure entre le vert de malachite et le violet de méthyle. Comme le montre cette figure, le vert de malachite et le violet de méthyle ont, respectivement, deux et trois groupes diméthylaminés entre lesquels une charge électrique positive est mise en résonance. Ce fait empêche la localisation d'une charge électrique et amènera, par conséquence, la diminution du pouvoir de la combinaison du colorant avec un ion de sulfate de dodécyl. En outre, plus les structures mises en résonance sont nombreuses, plus le degré de localisation d'une charge sera faible. Alors, le complexe se forme suffisamment en solution pour que l'on puisse observer sa floculation dans le cas du vert de malachite et ne l'est pas dans le cas du violet de méthyle.

Lorsque la quantité de S.D.S. augmente davantage en solution, la combinaison de l'ion de sulfate de dodécyl au complexe a lieu et ce complexe commence à se disperser.

Floculation et défloculation des colorants directs.—Il est bien connu que les molécules de colorant direct se forment l'agrégat dans l'eau, donc l'interaction entre le colorant et le surfactif doit être, dans ce cas, celle entre l'agrégat des molécules de colorant, que nous appellerons le micelle de colorant, et les ions de surfactif.

Cette considération nous amène à conclure que le mécanisme de la floculation du colorant direct sera le même que celui qui a été proposé par les présents auteurs pour la floculation des particules colloïdales par le surfactif[4]. C'est-à-dire, la surface du micelle de colorant perd l'affinité pour l'eau, et il en résulte la floculation.

La tendence vers l'agrégation dépend de la structure chimique du colorant. Pour des colorants directs employés dans ce travail, cette tendence augmente dans l'ordre suivant[5]:

Chrysophénine G < rouge de congo < benzopurpurine 4B.

On pourra expliquer plausiblement les résultats expérimentaux obtenus pour la défloculation, si l'on présume qu'un micelle de colorant est partagé en certains submicelles ou en molécules individuelles par l'addition d'une grande quantité de surfactif et que le micelle de la benzopurpurine est partageable le moins facilement. En d'autres termes, on présume que la défloculation du colorant direct succède au partage du micelle de colorant par le surfactif.

La dispersion du submicelle, correspondant à celle dans la première zone de défloculation, sera due à l'adsorption des ions de surfactif, orientant leur groupe ionique vers l'eau, sur la surface hydrophobique du submicelle floculé.

Lorsque la concentration de surfactif

3) K. Meguro, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **77**, 72 (1956).

4) K. Meguro et T. Kondo, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*,), **76**, 642 (1955).

5) T. Vickerstaff, "The Phsical Chemistry of Dyeing", Oxford Univ. Press, London (1954).

croît de plus en plus, le submicelle commence à se diviser. Les charges électriques qui ont été cachées apparaîtront alors et les ions de surfactif se déposeront sur ces charges. La deuxième zone de floculation paraît ici.

L'élévation de la température accélère le partage du micelle du colorant[5]. Ce fait causera la contraction de la première zone de défloculation, qui a été observée dans le cas de la chrysophénine G.

Le mécanisme de la défloculation dans la deuxième zone sera le même que celui suggéré pour les colorants acides ou basiques.

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Catalytic Hydrogenation of Aromatic Nitriles

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(Received February 17, 1959)

Catalytic hydrogenation of various aromatic nitriles has been investigated using nickel-copper-kieselguhr catalyst in vapor phase. An earlier study has been made by P. Sabatier[1], but it was only reported that benzonitrile was reduced to toluene and ammonia, while a different result was presented by A. Frébault[2]. Systematic study in this field has never been made and the mechanism of hydrogenation of nitriles has not yet been thoroughly established, although some views have been presented during the past half century[3]. In this paper, results of a systematic study on the catalytic hydrogenation of various aromatic nitriles are presented. The effect of various substituents in aromatic ring is discussed, along with the factor of promotion and retardation in hydrogenation. Further, the mechanism of the hydrogenation of nitriles has been investigated and some views are presented.

1) **Hydrogenation of Aromatic Nitriles in Vapor Phase.**—It was previously reported that nitrile is hyrogenated to methyl compound and ammonia in vapor phase[1] (1), whereas to amines in liquid phase[3] (2).

$$RCN \xrightarrow{H_2} RCH_3 + NH_3 \qquad (1)$$

$$RCN \xrightarrow{H_2} RCH_2NH_2,\ (RCH_2)_2NH \qquad (2)$$

The original purpose of the present study was to investigate whether or not aromatic nitriles of any kind undergo hydrogenolysis to methyl compounds in vapor phase. Various aromatic nitriles listed in Table I have been hydrogenated. The vapor of nitrile, mixed with an excess of hydrogen, was passed over a catalyst in a reaction tube, which was heated to an appropriate temperature between 200 ~350°C in an electric furnace. The catalyst, which consists of 60% of reduced nickel and 40% of reduced copper, was prepared according to Sabatier's method[1], and supported on purified kieselguhr. Representative experimental results of the hydrogenations are summarized in Table I. As seen in the table, it has been proved that aromatic nitriles are generally hydrogenated to the corresponding methyl compounds according to Formula 1 except for some special cases. However, it is important to note that this cleavage reaction of the nitrile group could not be complete unless sufficient condition for hydrogenation was given[4].

It is now apparent that the reaction temperature at which the hydrogenolysis is effectively carried out is governed by the nature of the compound to be hydrogenated. A well defined range of temperature for the efficient cleavage reaction was found for each compound. It has been found that, in general, a scission of C–C bond between nitrile group and

1) P. Sabatier and J. B. Senderens, *Compt. rend.*, **135**, 226 (1902); **165**, 309 (1917); **140**, 482 (1905).
2) M. A. Frébault, ibid., **140**, 1036 (1905).
3) C. Paal and J. Gerum, *Ber.*, **42**, 1153 (1909); G. Mignonac, *Compt. rend.*, **171**, 114 (1920); J. v. Braun et al., *Ber.*, **56**, 1988 (1923); K. W. Rosenmund et al., ibid., **58**, 51 (1925); K. Kindler, *Ann.*, **485**, 113 (1931); R. Juday and H. Adkins, *J. Am. Chem. Soc.*, **77**, 4559 (1955).
4) M. Obata, K. Watanabe and K. Hata, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **78**, 116 (1957).

TABLE I. CATALYTIC HYDROGENATION OF AROMATIC NITRILES IN VAPOR PHASE

Catalyst: ca. 25 g (mixture of NiO and CuO (Ni 60%, Cu 40%) 11 g., purified kieselguhr 14 g., reduced at ca. 300°C before the hydrogenation experiment)
Flow velocity of hydrogen ca. 0.1 l./min.; Flow velocity of sample 0.05~0.1 g./min.

Expt. No.	Nitriles	Temp. (°C)	Time (hr.)	Methyl compounds and yields (%)		Yields of ammonia (%)	Other products (%)	Lit.
1.	Benzonitrile	250	1⅔	Toluene	(87)	100		12
2.	Benzonitrile	358	3½	Toluene	(29)	76	Benzene (39)	12
3.	α-Naphthonitrile	270	3	α-Methylnaphthalene	(74)	97		1—3
4.	β-Naphthonitrile	240	3½	β-Methylnaphthalene	(73)	74		4
5.	*p*-Tolunitrile	205	4	*p*-Xylene	(72)			5
6.	*o*-Tolunitrile	240	3½	*o*-Xylene	(87)	100		6, 17
7.	*p*-Nitrobenzonitrile	300	4⅓	*p*-Toluidine	(43)	92	Aminonitrile (32)	7
8.	*m*-Nitrobenzonitrile	250	2⅓	*m*-Toluidine	(56)	73	Aminonitrile (9)	8
9.	*o*-Nitrobenzonitrile	300	1¼	*o*-Toluidine	(17)	79	Aminonitrile (20) Aniline (48)	9
10.	*p*-Aminobenzonitrile	330	3	*p*-Toluidine	(80)	90	Aniline (5)	13
11.	*o*-Aminobenzonitrile	300	3	*o*-Toluidine	(9)	94	Aniline (40)	13
12.	Ethyl *o*-cyano-benzoate	260	2	—		15	Phthalimidine (74)	10
13.	Ethyl *p*-cyano-benzoate	280	2	Ethyl *p*-toluate	(70)	80		16
14.	*p*-Bromobenzonitrile	200~300	1½	—		0	Recovered nitrile	11
15.	*p*-Chlorobenzonitrile	250~350	1½	Toluene (small quantities)		35~60	Recovered nitrile	11
16.	Benzyl cyanide	240	3	Ethylbenzene	(34)	69	Toluene (12) β-Phenylethyl-amine (18)	14
17.	*p*-Hydroxy-benzonitrile	453	2¼	*p*-Cresol	(75)	100	Toluene (10)	15
18.	Salicylonitrile	363	6½	*o*-Cresol	(68)	80	Phenol (11)	18
19.	*p*-Methoxy-benzonitrile	240	1⅓	*p*-Cresyl methyl ether	(70)	100		22
20.	*o*-Methoxy-benzonitrile	300	2¼	*o*-Cresyl methyl ether	(73)	100		19
21.	2,6-Dimethoxy-benzonitrile	300	4	—		86	1,3-Dimethoxy-benzene (55) Recovered nitrile (13)	23
22.	*p*-Cyanobenzalde-hyde	280	2½	*p*-Xylene	(28)	60	Toluene (12)	24
23.	Terephthalo-nitrile	304	2⅓	*p*-Xylene	(46)	81	*p*-Tolunitrile (11)	20
24.	Phthalonitrile	310	1½			78	*o*-Tolunitrile (15) Polymerization	20
25.	Acetylmandelic acid nitrile	250	4½	Ethylbenzene	(70)	74	Acetic acid (68)	21
26.	2,4,6-Trimethyl benzonitrile	240	2½	Isodurene	(ca. 50)	60	Recovered nitrile (34)	25
27.	Cinnamonitrile	260	2½	Propylbenzene	(90)	100		26

1) K. Hata, *Bull. Inst. Phys. Chem. Research* (*Tokyo*), **23**, 224 (1944). 2) K. Hata, ibid., **23**, 296 (1944). 3) K. Hata, ibid., **24**, 1 (1945). 4) K. Hata, ibid., **24**, 34 (1945). 5) K. Hasegawa and K. Hata, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **72**, 54, (1951). 6) Y. Tanaka and K. Hata, ibid., **73**, 85 (1952). 7) K. Watanabe, ibid., **76**, 391 (1955). 8) K. Watanabe, ibid., **76**, 395 (1955). 9) K. Watanabe, ibid., **76**, 398 (1955). 10) K. Watanabe, ibid., **76**, 888 (1955). 11) J. Mukai, K. Watanabe and K. Hata, ibid., **76**, 1354 (1955). 12) M. Tanaka, K. Watanabe and K. Hata, ibid., **76**, 1392 (1955). 13) K. Watanabe, ibid., **77**, 221 (1956). 14) K. Watanabe, ibid., **77**, 977 (1956). 15) M. Tanaka, K. Watanabe and K. Hata, ibid., **77**, 980 (1956). 16) K. Watanabe, ibid., **77**, 1272 (1956). 17) M. Obata, K. Watanabe and K. Hata, ibid., **78**, 116 (1956). 18) M. Tanaka, ibid., **78**, 1385 (1957). 19) F. Iwamoto, K. Watanabe and K. Hata, ibid., **78**, 1390 (1957). 20) M. Tanaka, ibid., **79**, 1302 (1958). 21) M. Tanaka, ibid., **79**, 1318 (1958). 22—26) Unpublished.

aromatic ring occurs as shown in Formula 3, when the hydrogenation is carried out at higher temperature (e. g., Experiment No. 2).

$$RCN \xrightarrow{H_2} RH + CH_3NH_2^* \quad (3)$$

The data given in Table I, are the results of the hydrogenation which give the best yield of the methyl compound among several experiments carried out under various conditions, especially under various reaction temperatures (except for Experiment No. 2). On the other hand, ammonia, which was liberated from the nitrile group during hydrogenation, was introduced to normal sulfuric acid solution and was determined by a titration with baryta water. The yield of ammonia suggests the degree of the cleavage reaction of the nitrile group. When the condition of hydrogenation is changed, somewhat different results can be observed for each compound. It is significant that the cleavage of the nitrile group is largely dependent upon the kinds and the positions of substituents in the aromatic ring.

Besides the normal cleavage reaction of nitriles, various side reactions were observed. For example, reductive cyclization was remarkable in the reaction of ethyl *o*-cyanobenzoate[5]. Sometimes, the side reaction was so complicated that the products could not be identified.

1) Effect of Substituents in Aromatic Ring on the Hydrogenation of Nitriles.— It is very difficult to estimate the effect of substituents on the hydrogenation of the nitrile group, because catalytic reaction is complicated with many factors. Nevertheless, it is conceivable that the relative reactivity of the cleavage reaction may be estimated by comparing the yields of the products, although a vapor phase hydrogenation is carried out ordinarily under such a drastic condition that it may cause undesirable side reactions. In general, it has been proved that a substituent in the aromatic ring exhibits both electronic and steric effects on the hydrogenation of the nitrile group. Any substituent seems to depress the hydrogenation of the nitrile group.

As for the electronic effect, electron-releasing substituents give less effect, while electron-attracting substituents such as nitro, cyano, ethoxycarbonyl and aldehyde groups restrain the hydrogenation of the nitrile group remarkably. However, the effect due to the electronic characteristics of the substituent is not always observed clearly since the catalytic hydrogenation is also governed by many other complicated factors.

In the catalytic reaction, it is the first requisite for the initiation of the reaction that the compound should be adsorbed on the surface of the catalyst. This consideration has led to the inference that the nitrile group will be unfavorably hydrogenated, if another substituent in the same ring undergoes competitive hydrogenation or interferes with the adsorption of the nitrile group on the catalyst by steric effect. As for the steric effect, it is expected that the nearer the substituent to the nitrile group is, the larger is its effect. This effect is observed distinctly about nitro, amino, cyano, hydroxyl and ethoxycarbonyl groups, and may be expressed in terms of "ortho effect" in hydrogenation. When two substituents are introduced in both ortho positions beside the nitrile group, a greater steric effect is observed (Table I, Experiments No. 21 and 26). This "ortho effect" could not be obviously observed in the previous studies of hydrogenation in liquid phase. Further investigation of this effect should be made in connection with a mechanism of the reaction on the surface of catalyst.

A special interfering effect of the nitro and amino groups on the hydrogenation of the nitrile group, has been studied in particular[6]. It was first pointed out in the liquid phase hydrogenation by H. Rupe[7], that the nitro group has an interfering effect on the hydrogenation of the nitrile group, and it was shown extensively that the nearer the nitro group is to the nitrile group, the greater is the effect. Hydrogenation of nitro and aminobenzonitriles in vapor phase also gave less yield of the hydrogenolysis products (Table I, Experiments No. 7—11). In order to solve this problem, some experiments on mixed hydrogenation were made. The vapor of benzonitrile was mixed with that of nitrobenzene, aniline or water, and the mixture was hydrogenated as usual. On the other hand, benzonitrile was hydrogenated on the catalyst which had been previously used for the hydrogenation of nitrobenzene or aniline. The results of the experiments

* Methylamine may be further hydrogenated to methane and ammonia in high reaction temperature.

5) K. Watanabe, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **76**, 888 (1955).

6) K. Watanabe, ibid., **77**, 225, 1741 (1956).

7) H. Rupe et al., *Helv. Chim. Acta*, 8, 832, 838 (1925).

TABLE II. MIXED CATALYTIC HYDROGENATION OF AROMATIC NITRILES

Expt. No.	Method	Compounds (g.)	Temp. (°C)	Time (hr.)	Main products and yields (%)		Other products*
1.	A	Benzonitrile (7) + Nitrobenzene (7)	250	3½	Toluene	(61)	Aniline (74%)
2.	B	Benzonitrile (6)	250	2¼	Toluene	(60)	
3.	A	Benzonitrile (8) + Water (3)	250	2	Toluene	(59)	Amines (+) Recovered nitrile
4.	A	Benzonitrile (6) + Aniline (6)	250	3	Toluene	(62)	Recovered aniline
5.	C	Benzonitrile (6)	250	2	Toluene Dibenzylamine	(39) (18)	Benzylamine (+) Tribenzylamine (+) Recovered nitrile (18%)
6.	A	*p*-Aminobenzonitrile (6.6) + Water (3)	330	2	*p*-Toluidine	(59)	Recovered nitrile (15%) Aniline (+)

Method A: The mixture of two substances was hydrogenated.

Method B: Catalyst that was used beforehand for the hydrogenation of nitrobenzene (5 g.) was used successively.

Method C: Catalyst that was used beforehand for the hydrogenation of aniline (5 g.) was used successively.

* Products marked with (+) were detected in small quantities.

TABLE III. CATALYTIC HYDROGENATION UNDER INSUFFICIENT CONDITIONS

Expt. No.	Catalyst (g.)	Compounds (g.)	Temp. (°C)	Flow velocity of sample (g./hr.)	Products and yields (%) Methyl compds.	Prim. amine	Sec. amine	Tert. amine	Ammonia	Recovered sample (%)
1.	30	*o*-Tolunitrile (6.7)	240	3	87	—	—	—	100	—
2.	10	〃 (5.9)	260	2	70	1	4	—	91	10
3.	10	〃 (6.0)	〃	6	37	3	8	—	64	37
4.	2	〃 (4.0)	〃	4	16	4	12	—	44	45
5.	0.7	〃 (5.1)	〃	2.5	0	9	11	—	17	61
6.[a]	25	〃 (6.3)	〃	3	62	2	3	—	63	22
7.	10	Benzonitrile (3.0)	260	5	52	2	14	2	68	8
		(12.0)	〃	5	47	7	17	3	70	17
		(5.0)	〃	6	32	6	25	5	64	18
8.	2	〃 (4.0)	〃	4.5	34	7	24	—		18
9.[b]	2	Benzylamine (5.6)	260	6	27	—	27	—		30

a) Flow velocity of hydrogen was diminished to 1.3 l./hr.: in other experiments, excess of hydrogen was used (flow velocity 5~6 l./hr.)

b) Cf. Table V, Experiment No. 6.

are shown in Table II. From these results, it is inferable that the nitro group is first reduced to the amino group and suppresses the hydrogenation of the nitrile group by a competitive reaction. It is further proved that the amino group produced from the nitro group acts poisonously for the catalytic activity (cf. Section 4). However, the hydrogenolysis of *p*-aminobenzonitrile could not be affected by the *p*-substituted amino group. This can be interpreted by the steric ineffectiveness of the *p*-substituted amino group as a poison for the catalyst.

3) **Investigation of Hydrogenation Mechanism of Nitriles.**—The investigation of the behavior of various nitriles in the hydrogenation has led to the study of hydrogenation mechanism of nitriles, which is complicated owing to the presence of secondary products. Generally, it has been known[3] that the main process of the hydrogenation of nitriles may be shown as follows:

$$RCN \rightarrow RCH=NH \rightarrow RCH_2NH_2 \rightarrow RCH_3+NH_3 \quad (4)$$

$$RCH=NH+RCH_2NH_2 \rightarrow RCH=NCH_2R \rightarrow (RCH_2)_2NH \quad (5)$$

$$3\,RCH=NH \rightarrow RCH(N=CHR)_2 \rightarrow RCH=NCH_2R \rightarrow (RCH_2)_2NH \quad (6)$$

It is conceivable that the course of the

TABLE IV. HYDROGENATION OF BENZYLAMINE AND DIBENZYLAMINE

Expt. No.	Compounds (g.)		Temp. (°C)	Time (hr.)	Products and yields[b] (%)		Other products
1.	Benzylamine	(7.3)	250	2	Toluene	(66)	Oil of high boiling point
2.	Benzylamine	(10.0)	360	3	Toluene	(46)	Benzene (9%)
3.[a]	Benzylamine	(7.2)	250	1⅔	Toluene	(81)	
4.	Dibenzylamine	(6.0)	300	2½	Toluene Benzylamine	(34) (+)	Unidentified by-product
5.	Dibenzylamine	(7.3)	350	3½	Toluene Benzylamine	(44) (+)	Unidentified amine
6.	Benzylamine Benzonitrile (Mixture)	(4.0) (4.2)	250	3¼	Toluene (4.3 g.) Benzylamine Dibenzylamine	(68)[c] (+) (+)[d]	Recovered nitrile

a) Before the hydrogenation, 5 mg. of thiophene dissolved in 0.1 g. of benzene was vaporized and passed over the catalyst (cf. Table V, Experiment No. 6).
b) (+) denotes detectable but unestimated.
c) The yield of toluene from benzylamine is also calculated as the yield from benzonitrile.
d) Very small amount: When benzonitrile was hydrogenated with the catalyst treated with benzylamine beforehand, about the same amount of dibenzylamine was obtained (Table V, Experiment No. 10).

TABLE V. EFFECT OF THIOPHENE AND SOME BASES ON THE HYDROGENATION OF NITRILES

Expt. No.	Compounds (g.)		Additional compounds[a] (g.)	Temp. (°C)	Time (hr.)	Products and yields (%) Methyl compds.	Prim. amine	Sec. amine	Recovered sample (%)	Remarks[b]
1.	Benzonitrile	(8)	None	250	1⅔	88	–	–	–	Catalyst 25 g.
2.	〃	(5)	Thiophene (0.003)	250	2	82	+	–	–	Catalyst 10 g.
3.	〃	(5)	〃 (0.2)	250	2	14	–	–	84	Catalyst 10 g.
4.	〃	(7)	〃 (2.0)	250	1½	28	–	–	67	
5.	〃	(7)	〃 (0.005)	350	2	30	+	–	7	Benzene (42%)
6.	Benzylamine	(6)	〃 (0.003)	250	1½	66	–	21	12	Catalyst 10 g.
7.	Benzonitrile	(7.7)	Ammonia	250	2½	69	+	+	–	
8.[c]	〃	(7.1)	〃	250	2	14	14	13	43	
9.	〃	(6)	Aniline (5)	250	2	39	+	18	18	Tribenzylamine
10.	〃	(7.4)	Benzylamine (6.4)	250	3	66	+	+	+	
11.	〃	(10.8)	Dibenzylamine (7.5)	250	2¼	18	14	30	19	
12.	〃	(7)	〃 (2.0)	355	2½	16	11	–	11	Benzene (47%)
13.	〃	(7)	Pyridine (1.0)	250	2⅓	78	+	+	–	

a) The nickel catalyst was previously treated with the vapor of these compounds, and then the nitrile was hydrogenated.
b) 25 g. of catalyst was used except for Experiments No. 2, 3 and 6.
c) The mixture of benzonitrile and ammonia was hydrogenated.

reaction is nearly the same whether in liquid phase or in vapor phase although some differences are found. Some factors in the hydrogenation may forcibly control the process of these reactions. The normal process of the hydrogenation of nitrile in vapor phase follows the course shown in Formula 4, and other side reactions or interruption of the process 4 may be caused by inadequate conditions of the hydrogenation. Such a hydrogenation under insufficient conditions may give ample facilities for the study of hydrogenation mechanism. Therefore, some hydrogenation experiments were tried intentionally under insufficient conditions (quantity of catalyst, feeding velocity of sample and hydrogen, etc.)[4]. It has been shown that the course of the reaction can be controlled in the expected way according to the condition of the hydrogenation. The examples of these experimental results are summarized in Table III.

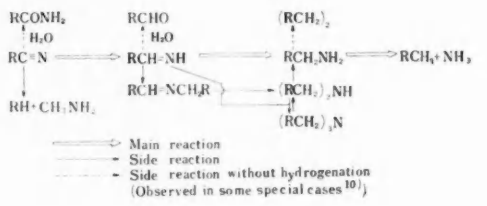
In the hydrogenation of *o*-tolunitrile (Experiments No. 1—5), the yield of the methyl compound through course 4 decreased according to the decreasing quantity of catalyst used, alternatively yielding the increasing quantity of primary and secondary amines. When a small amount of hydrogen was fed during the hydrogenation, a similar result was obtained (Experiment No. 6). In Experiment No. 7, benzonitrile was hydrogenated in three portions successively on the same catalyst, and the products were collected separately for every portion. The components of the reaction products were varied according to the proceeding of the reaction, whereby the changing feature of the reaction was observed.

To ascertain the hydrogenation mechanism, the investigation of the behavior of the intermediate compounds in the process is useful. Thus, the further hydrogenation of amines, which have been found to be intermediate of the process, was carried out[8]. The results of the experiments are summarized in Table IV. When benzylamine was hydrogenated, toluene was obtained and no dibenzylamine was found. But the yield of toluene from benzylamine by the hydrogenation was less than that from benzonitrile, and a small quantity of unidentifiable by-product was obtained from benzylamine. It has been found that benzylamine was smoothly hydrogenated and toluene was obtained in good yield, when a small quantity of thiophene was added to the catalyst (Experiment No. 3). On the other hand, when dibenzylamine was hydrogenated, toluene was obtained in considerable yield, along with a small amount of benzylamine and other unidentified by-product.

It was reported previously by v. Braun[3] that the secondary amine is formed by interaction between a primary amine and an aldimine when aromatic nitrile is hydrogenated in liquid phase (process 5). According to the present investigation in vapor phase, it is evident that dibenzylamine can scarcely be obtained by the hydrogenation of benzylamine, or of the mixture of benzonitrile and benzylamine. It is assumed subsequently that the formation of dibenzylamine in the hydrogenation under insufficient conditions, proceeds through hydrobenzamide and Schiff base as an intermediate according to Formula 6.

It has been found that, when aromatic nitriles are hydrogentated in vapor phase at a higher temperature, the ordinary hydrogenation to methyl compound (reaction 1) is generally accompanied with the hydrogenolysis of C–C bond between the nitrile group and aromatic ring (reaction 3). It has been proved that this cleavage of C–C bond occurs mainly before the hydrogenation of C–N bond does[9]. This cleavage reaction also occurs even at a temperature not so high, when the hydrogenation of the nitrile group happens to be interfered with by the effect of other substituents (Table I, Experiments No. 9 and 11). The cleavage of this type is observed especially in some ortho-substituted benzonitriles (Table I, Experiments No. 21 and 26).

Considering the results of these experiments, the hydrognation mechanism of aromatic nitriles in vapor phase is assumed to be as follows:



8) K. Watanabe, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **78**, 1478 (1957).

9) M. Tanaka, K. Watanabe and K. Hata, ibid., **76**, 1392 (1955).

10) K. Watanabe, ibid., **76**, 391, 398 (1955); K. Watanabe, ibid., **77**, 1272 (1956); K. Hasegawa and K.Hata, ibid., **72**, 54 (1951).

TABLE VI. EFFECT OF THIOPHENE ON THE HYDROGENATION OF NITRILE IN LIQUID PHASE

Catalyst: U-Ni-B; Sample: Benzonitrile (7.2 g.); Solvent: 99% Ethanol; Room temperature

Expt. No.	Weight of thiophene (g.)	Hydrogen absorbed (%)	Time (hr.)	Products and yields (%)		
				Prim. amine	Sec. amine	Aldehyde
1.	0	90	1⅔	47	23	11
2.	0.007	93	2⅙	61	13	11
3.	3.5	89	11	56	11	15

4) Factors for Promotion and Retardation in Hydrogenation of Nitriles.—It has been widely known that the result of the hydrogenation reaction varies according to the character of the catalyst, which can be controlled by the addition of appropriate promoter or poisonous matter. The promotion or retardation of the hydrogenation was also observed in aromatic nitriles. The effect of various substances on the character of the nickel catalyst has been investigated[8], and the results of these experiments are summarized in Table V. When benzonitrile was hydrogenated with nickel catalyst which was previously treated with a small amount of thiophene, toluene was obtained in high yield, little by-product being found (Experiment No. 2). On the contrary, when the catalyst was previously treated with ammonia, amine or pyridine, the formation of toluene was suppressed and considerable amounts of by-products were obtained (Experiments No. 7—13). In some experiments, the mixture of benzonitrile and some other basic substances was hydrogenated with the ordinary nickel catalyst, and the results were similar to those in Table V (except the experiment with ammonia, cf. Experiments No. 7 and 8). A similar effect of thiophene has been observed in the liquid phase hydrogenation of benzonitrile (shown in Table VI)[11].

As the result of these experiments, the addition of basic substances (such as amine) has been found to cause retardation of the hydrogenation of nitrile. On the other hand, it has been found that the addition of a small quantity of thiophene causes promotion and increases the yield of the methyl compound, whereas the formation of secondary products is considerably suppressed. Thus, it is evident that the suitable amount of thiophene on the catalyst retards the side reaction of nitriles (e. g., the formation of secondary amine). This effect was especially remarkable in the case of hydrogenation under insufficient conditions. For example, toluene was obtained in high yield from benzonitrile, even when a small quantity of the catalyst was used (Experiment No. 2, compared with Experiment No. 7 in Table III). On the contrary, a large amount of thiophene acts as poison for all the various sorts of the reaction: a large quantity of the nitrile was recovered unchanged (Experiments No. 3 and 4).

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11) T. Okazawa, K. Watanabe and K. Hata, unpublished.

On the Dissolution of Na_2O-CaO-SiO_2 Glass in Acid and in Water

By Shoji TSUCHIHASHI and Eiichi SEKIDO

(Received February 26, 1959)

The "chemical durability of glass" is one of the research items of great academic interest, and of leading technical importance as well. Accordingly, there have been many papers published on this subject.

The usual way of representing the results of durability tests is to express them in the equivalent concentration of sodium oxide leached out from the glass surface; sometimes from glass powder to accelerate the attack on glass, or from the glass container itself to make the data more practical. For many purposes this way of presenting data is very useful, because the varying alkalinity of the solution stored in a glass container is often a matter of serious concern.

In multi-component glasses, sodium oxide is not the only substance which passes into solution, even in the initial stage when the silica network remains unchanged. Investigating the change of interference colors produced by the changing thickness of the silica-layer remaining on the surface of some flint glasses immersed in nitric acid solution, the author could confirm the fact that the chemical attack proceeds through the exchange reaction between cations such as Na^+, K^+ and Pb^{2+} in glass on the one hand and H^+, or H_3O^+ in solution on the other[1]. Moreover, the exchange between Na^+, K^+ in glass and H^+ in solution takes place at a rate far greater than that between Pb^{2+} in glass and H^+ in solution, so that the rate of diffusion of Pb^{2+} through glass network determines the rate of reaction.

In studying the mechanism of chemical attack on glass by using soda-lime-silica glass which is simpler in composition and of more practical importance, the optical method fails in its object, because both the rate of reaction and the difference in refractive index between the surface layer and the body are smaller than when we use flint glass.

Hence, in order to draw a clear picture of the complete set of chemical reactions, the components leached out from glass by the conventional powder method were completely analyzed.

1) S. Tsuchihashi, This Bulletin, **24**, 161 (1951).

Experimental Methods

Preparation of the Solution for Analysis. —1) *Sample.*—The glass plates of composition given in Table I were crushed in a percussion mortar, and the powder was sieved to classify it into three meshes, namely, 16~20 (0.833~0.991 mm.), 20~24 (0.701~0.833 mm.), 24~32 (0.495~0.701 mm.), washed thoroughly with methanol to remove all fine particles adhering to the grains, and finally dried at 120°C.

TABLE I. COMPOSITION OF GLASS (weight %)

SiO_2	Na_2O	CaO	MgO	$Fe_2O_3+Al_2O_3$
73.64	13.12	8.44	2.37	2.37

2) *Acid solution.*—As it is necessary to deal exhaustively with an extremely small amount of ions, the water used for the experiments was completely demineralized by treating it successively with ion-exchange resins. This treatment was used also for preparing hydrochloric acid and sulfuric acid solutions, the concentrations of which were 1 N throughout the experiments.

3) *Apparatus.*—The apparatus used for the leaching out experiments is shown in Fig. 1. It is a three-necked flask with a stirrer, both of which are made of Pyrex glass.

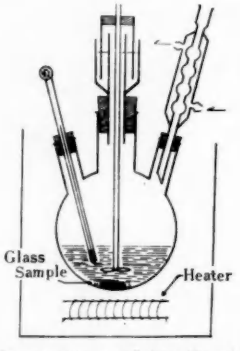

Fig. 1. Apparatus used for the durability test.

4) *Procedure.*—1.00 g. of the glass powder was accurately weighed out and transferred into the flask containing 100 ml. of reagent. Under continuous stirring the temperature was raised as quickly as possible to 100°C, at which it was kept

constant for one or three hours, and then the flask was cooled to room temperature. The solution was separated carefully from the glass powder and subjected to chemical analysis.

A series of blank tests were made in order to determine the amount leached out from the container wall and from the stirrer. The figures obtained, although negligibly small, were subtracted from the results in order to obtain the actual net values.

Chemical Analysis of the Solution.—I. *Silica.*—In order to determine an extremely small amount of silica which had passed from the glass into the liquid, the spectrophotometric method based on the measurement of yellow or blue molybdo-silicic acid was used. There are, however, some points which should be made extremely clear in order to get reliable results. It is known that the color developed changes with the state of existence of silica in solution, namely, whether it is in ionic state, in molecular state or in colloidal state[2-5]. The following conditions should be taken into account.

1) *pH value.*—Quite recently Narita[6] investigated the relation between the quantity of silica in ionic state and the pH of sodium silicate solutions with the result shown in Fig. 2. Since his experiments covered higher percentages of silica than in the present instance, the authors made experiments on the solutions containing smaller amounts of silica, whose compositions are given in Table II.

The silica content was exactly 5 p. p. m. after 6 hr. and 5 p. p. m. after 6 days in pH 12 solution, but was reduced to 0.5 p. p. m. in a 1 N sulfuric acid solution. By adding Ca^{2+} to the solution the

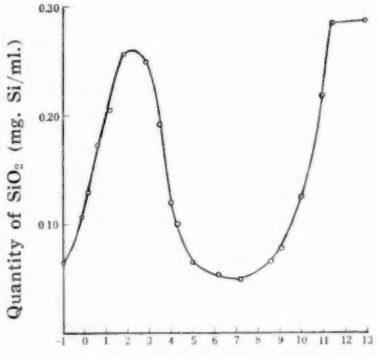

Fig. 2. The relation between the quantity of SiO_2 in ionic state and the pH of solution (after Narita).

TABLE II. DETERMINATION OF SiO_2 INFLUENCED BY OTHER ELEMENTS

Sample solutions	Value of measurements	
	After 6 hr.	After 6 days
5 p.p.m. SiO_2 in 1N H_2SO_4	5 p.p.m.	0.5 p.p.m.
5 p.p.m. SiO_2+5 p.p.m. Ca^{2+}, in 1 N H_2SO_4	5	0
5 p.p.m. SiO_2 in pH 12 solution	5	5
5 p.p.m. SiO_2+5 p.p.m. Ca^{2+}, in pH 12 solution	5	2.9

quantity of ionic silica was reduced; for instance, to 0 in a 1 N sulfuric acid solution, and to 2.9 in an alkaline solution of pH 12. From these observations it may be concluded that the quantity of ionic silica does not depend on the pH of that solution alone. As it has already been shown that the optimum pH value to determine the amount of silica is 1~1.6, we also followed these conditions in performing our experiments.

2) *Quantity of ammonium molybdate.*—The absorption spectra of the solutions, one containing 2 p. p. m. of silica and various amounts of molybdate and the other 20 p. p. m. of silica and various amounts of molybdate, were measured with the result that the addition of 5 ml. of 10% solution of molybdate to 50 ml. solution containing silica gave the greatest sensitivity to the spectra, and that the addition of a larger amount than 5 ml. brought about an undesirable influence[5,7].

3) *Wavelength.*—The published photometric procedures have proved to be of no practical use for measuring the absorption of the yellow molybdo-silicic acid at the optimum wavelength. The recommended wavelengths in millimicrons were: 370[8], 380[7], 390[9], 390 to 400[10], 400[11], 405[12], 416[6,7,13], 420[14], 425[15] and 436[16]. Taking into account these facts, the authors used 410 mμ ("yellow" method) and 810 mμ ("blue" method).

4) *Calibration curve.*—Beer's law was applicable whithin the range from 0 to 60 p. p. m. of silica, and the authors used this calibration curve for the quantitative determination of silica.

We measured the absorbance of the solution as soon as possible after adding the ammonium molybdate to that solution to prevent the influence of Ca^{2+} and other ions. Moreover, in order to examine whether or not any trace of silica might escape as colloid without forming silico-molybdate, alkali was added to the solution to digest the last trace of colloid before it was subjected to analysis.

2) F. Aoki, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **72**, 17 (1951).
3) T. Okura, ibid., **72**, 927 (1951).
4) Y. Iwasaki et al., ibid., **75**, 857 (1954).
5) M. A. Desesa and L. B. Roger, *Anal. Chem.*, **26**, 1278 (1954).
6) K. Narita, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **76**, 460 (1955).
7) K. Narita, ibid., **77**, 271 (1956).
8) J. Hure and T. Ortis, *Bull. soc. chim. France*, **16**, 834 (1949).
9) R. Guenther and R. H. Gale, *Anal. Chem.*, **22**, 1510 (1950).
10) U. T. Hill, ibid., **21**, 589 (1949).
11) M. Armand and J. Berthaux, *Anal. Chim. Acta*, **5**, 380 (1951).
12) J. R. Boyd, *Anal. Chem.*, **24**, 805 (1952).
13) O. P. Case, *Ind. Eng. Chem., Anal. Ed.*, **16**, 309 (1944).
14) D. Rozental and H. C. Campbell. idid., **17**, 222 (1945).
15) G. N. Cade, ibid., **17**, 372 (1954).
16) H. Pinsl, *Z. Metallkunde*, **27**, 107 (1935).

The results obtained with such treatment and those without it were quite the same, which proves that the present method is satisfactory.

II. *Sodium Oxide.*—Sodium oxide was determined by flame photometry using the spectral line at 589 mμ. As long as the concentration of alkali ions was in the order usually found in the durability tests, all substances except acids[17] were found to be harmless. The disturbance of acids was taken into full account, and the calibration curves were used to prevent the data from being influenced by coexisting anions.

III. *Calcium Oxide.*—Calcium oxide was determined by flame photometry using a calcium oxide band spectrum at 554 mμ. As it was found necessary to make clear the influence of coexisting ions on the result, a series of preliminary experiments were carried out.

1) *Influence of sodium ion.*—A 5 p. p. m. calcium standard solution containing 0 to 100 p. p. m. Na^+ and a 1 p. p. m. solution containing 0 to 20 p. p. m. Na^+ were aspirated to observe the change of the flame intensity, and it was possible to confirm the fact that there was no detectable influence of coexisting Na^+ so far as its concentration did not exceed 15 times the amount of Ca^{2+}.

2) *Influence of iron(III) ion.*—Carrying out the same experiments as the above using a 20 p.p.m. calcium standard solution containing 0 to 50 p.p.m. Fe^{3+}, it was recognized that the limiting concentration of Fe^{3+} was 0.5 times the amount of Ca^{2+}. As the amount of Fe^{3+} in the durability tests never exceeded this limiting value, the influence of coexisting Fe^{3+} may be ignored.

3) *Influence of silica.*—The change of the flame intensity of a 2 p. p. m. calcium standard solution containing silica (up to 5, 10 and 20 p.p. m., respectively) is shown in Figs. 3, 4 and 5. The curves show a general trend indicating that the flame intensity was reduced at first by the addition of silica and brought, by further addition, to a constant value approximately at the point

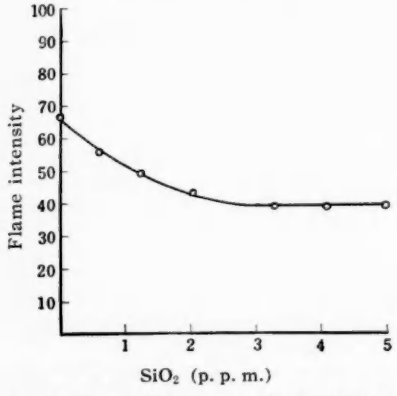

Fig. 3. Flame intensity of Ca^{2+} containing SiO_2
(Ca, 2 p. p. m.; SiO_2, 0~5 p. p. m.)

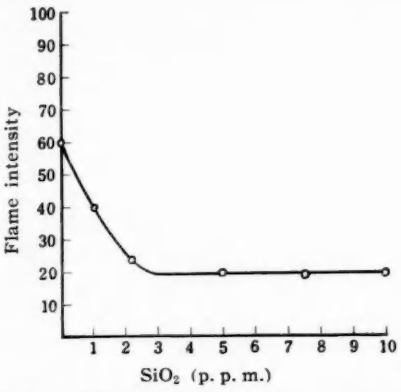

Fig. 4. Flame intensity of Ca^{2+} containing SiO_2
(Ca, 2 p. p. m.; SiO_2, 0~10 p. p. m.)

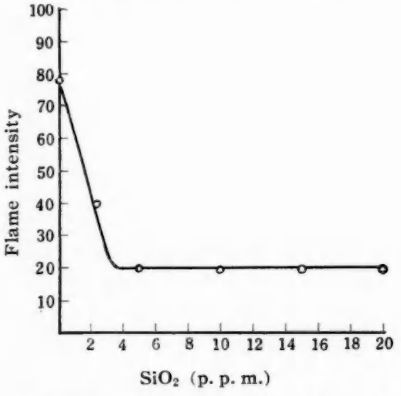

Fig. 5. Flame intensity of Ca^{2+} containing SiO_2
(Ca, 2 p. p. m.; SiO_2, 0~20 p. p. m.)

corresponding to the composition Ca : SiO_2=2 : 3. Thus, for the solution containing silica more than 3/2 of calcium, the calibration curve was drawn by analyzing the solution containing a known quantity of Ca^{2+}.

4) *Influence of acids.*—The disturbance of acids[18] was taken into full account and the calibration curves were made to make the results free from the influence of acids.

Results and Discussion

The data obtained by the durability tests are listed in Table III. The figures indicate that much larger amounts of silica were clearly leached out by water than by acids, and that silica probably placed a check on the rate of dissolution. In

17) P. Portor and C. Wyld, *Anal. Chem.*, **27**, 733 (1955).

18) S. Ikeda, *J. Chem. Soc. Japan, Chem. Sec.* (*Nippon Kagaku Zasshi*), **78**, 1434 (1957).

TABLE III. DURABILITY OF Na_2O-CaO-SiO_2 GLASS

Solution	Time (hr.)	Particle size (mesh)	Amount leached out in mg./100 ml. SiO_2	Na_2O	CaO	Na_2O/SiO_2
H_2O	1	16~20	0.20	0.06	0.01	0.29
		20~24	0.47	0.10	0.04	0.21
		24~32	0.68	0.18	0.04	0.25
	3	16~20	0.40	0.08	0.02	0.20
		20~24	1.05	0.21	0.05	0.20
		24~32	2.10	0.37	0.09	0.18
1N HCl	1	16~20	0.05	0.04	0.01	0.80
		20~24	0.09	0.08	0.04	0.89
		24~32	0.13	0.11	0.08	0.83
	3	16~20	0.06	0.05	0.02	0.80
		20~24	0.12	0.09	0.05	0.80
		24~32	0.20	0.16		0.80
1N H_2SO_4	1	16~20	0.10	0.06	0.07	0.58
		20~24	0.15	0.13	0.05	0.87
		24~32	0.20	0.17	0.07	0.83
	3	16~20	0.12	0.10		0.86
		20~24	0.20	0.15		0.73
		24~32	0.35	0.19		0.55
The ratio in base glass (weight per cent)						0.18

every case, however, larger quantities of silica than those of sodium oxide, and much smaller quantities of calcium oxide than of the other two were found in the solution. As usual, the total amount of dissolved matters inceased in proportion to the length of time, and in inverse proportion to the grain size of the glass powder.

As for the ratio Na_2O/SiO_2, the figures in the sixth and last rows show that the solution had practically the same proportion of sodium oxide to silica as the base glass, and also that the attack of water on glass presumably caused the collapse of the whole structure. The acids did not seem to be so destructive to the network structure, since the ratios were always higher. This indicates that the exchange reaction between H^+ in solution and Na^+, Ca^{2+} in glass is governed by the rate of migration of the ions through the glass network to the surface.

The idea of the collapse of the whole glass structure is strongly supported by the experimental results obtained by Tieze[18] and others[20,21] who confirmed the successive exfoliation of the silica layer during the durability test. This was also proved by the gradual increase of the quantity of dissolved substances.

Action of Water on Glass. — Let us first focus our attention on the network former, silica, which has non-bridging oxygen bonded with Na^+, and try to explain why the ratio of components in the solution was practically the same as that in the base glass when it was attacked by pure water. For this purpose it will be convenient to consider the whole process in two separate stages, i. e., (1) the initial stage and (2) the depth action, although there is no sharp boundary-line between them.

The reactions in the initial stage are illustrated schematically in Fig. 6. At first there will be the migration of Na^+ from the glass into the liquid, which gives rise to the place exchange between H^+ and Na^+. In the meantime Na^+ in the glass

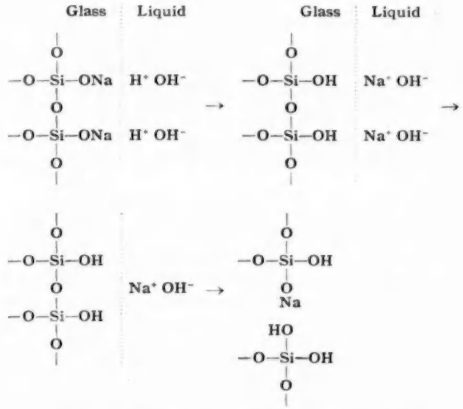

Fig. 6. Schematic representation of the chemical attack of water on glass surface.

19) P. Tieze, *Sprechsaal*, **61**, 809 (1928).
20) Tielsh and Zimmer, ibid., **66**, 285, 303, 319 (1933).
21) I. Sawai, M. Tashiro et al., *J. Ceram. Assoc. Japan* (*Yogyo Kyokai Shi*), **52**, 258 (1944).

will diffuse to the surface through the network without producing any appreciable influence upon its structure. The continuous supply of Na^+ from inside, however, will accumulate sodium hydroxide at the surface, which then will begin to attack the bonding oxygen to open the network, so that silica also passes into the solution with gradual increase in its concentration. Hence in the initial stage, more sodium oxide goes into the solution than silica; that is, Na_2O/SiO_2 is higher than that of the base glass. The high value of the ratio Na_2O/SiO_2 in the initial stage is shown in Table III.

In the second stage, the depth action extending inward from the surface should be taken into account. As the reaction proceeds through the mutual diffusion of Na^+ and H^+ (this H^+ can easily migrate through the network and can penetrate deep into the electron cloud of non-bridging oxygen), the structure of sodium silicate changes into that of silicic acid in the layer near the glass surface. Using sodium silicate or dense flint glass, existence of a sharp boundary-line at the surface may easily be observed under a microscope.

Protons penetrate into the electron cloud of oxygen. As a result, the change from ONa to OH brings about the change of electronic configuration around the non-bridging oxygen, which in turn induces the stress in the network. The strain thus developed in the surface layer induces the exfoliation of the skeleton en masse so that all glass components go completely into the solution, with the ratio of components remaining unchanged, whether they are in glass or are dissolved in the solution.

Attack of Acids on Glass.—It requires only a glance at Table III to observe the fact that there is a marked difference between the action of water and of acids. Two remarkable features may be pointed out:

(1) Acids accelerated the leaching of the metallic ions, while they reduced notably the rate of dissolution of silica.

(2) Each component showed different behavior when attacked by different acids.

The question why acids check the dissolution of silica may be answered quite easily, when we take into account the fact that silica network can not be opened until a sodium hydroxide attacks the bridging oxygen, since H^+ in acid solution has no power to open the silica network. In fact, vitreous silica is resistant to the attack of acids, though it is not resistant to that of alkalis.

In the glass containing modifier cations in its network there will be only the place exchange between H^+ and the metallic cation.

It should be noticed that, with a few exceptions, sulfuric acid was stronger than hydrochloric acid in the power of leaching out the cations, while the hydrogen ion concentrations of the solutions are in reverse order, namely,

$$HCl : 0.8 > H_2SO_4 : 0.55$$

This discrepancy may be explained by taking into account the nature of the negative charge distribution in the liquid at the boundary layer surrounding the glass particles. The negative charge of anions reduces the repulsion between the cations which are just going to leave the lattice points and those already existing in the solution. In short, the anion plays an important role in drawing out the cations from the glass network.

Summary

(1) The first step in the attack of water on glass is the exchange reaction between the proton and Na^+ on the glass surface. Sodium hydroxide thus produced in the boundary layer opens the Si–O–Si bond, and consequently silica passes into solution.

(2) When the exchange reaction between Na^+ in glass and H^+ in acid solution takes place, more metallic ions will be drawn out of the network owing to the influence of anions existing in the solution. Consequently more cations pass into the solution, while the silica network will be stabilized by acid so that the silica in the solution will be reduced remarkably.

The authors are indebted to Professor I. Sawai of Kyoto University for his advice and encouragement during the course of this research. Thanks are due also to Mr. S. Nakabayashi and Mr. Y. Nakatani who helped us with the laboratory work.

The cost of this research was defrayed by the Scientific Research Encouragement Grant from the Ministry of Education, to which the writers' thanks are due.

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Complexometric Titration of Rare Earth Elements. Dissolution of the Rare Earth Oxalate with Ethylenediaminetetraacetic Acid and Back Titration with Magnesium Sulfate

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(Received March 23, 1959)

Complexometric titration of the rare earth ions in solution has been studied widely by many investigators[1-3]. The rare earth oxalate is usually precipitated from a weak acid solution and used for the gravimetric determination of the rare earth elements. Oxalic acid is the most excellent precipitating reagent for the rare earth ion. However, according to the fact that the rare earth oxalate was dissolved in alkaline solution by adding the excess of ethylenediaminetetraacetic acid (EDTA), Marsh[4] studied the fractional precipitation of the rare earth elements, using a different solubility of each rare earth-EDTA-oxalate complex anion in successive decreases of pH of solution. The present authors found that the rare earth ion, in the presence of a large amount of the oxalate ions, could be determined by back titration of the excess of EDTA with standard magnesium sulfate solution using Eriochrome black T as indicator under certain conditions. Thus, the rare earth ion was precipitated as the oxalate, the precipitate was separated and an excess of standard EDTA solution was added to dissolve the precipitate. After the oxalate was completely dissolved, the excess of EDTA in the solution was back titrated with standard magnesium sulfate solution, using Eriochrome black T as indicator. The conditions of dissolution of the rare earth oxalate and of the back titration were studied in detail and the optimum conditions were obtained for the determination of the rare earth elements. This procedure affords good and accurate results for the determination of 1 to 5 mg. of rare earth elements contained in solution under certain conditions. Especially, it is more rapid and rather simpler than the usual gravimetric procedure.

Experimental

Preparation of Standard Solution and Reagents.—*Standard EDTA solution.*—A certain quantity of disodium ethylenediaminetetraacetate dihydrate (analytical grade pure) was dissolved in distilled water and standardized by titration with standard zinc chloride solution, using Eriochrome black T as indicator. Concentration of the standard EDTA solution: 0.01030 mol./l.

Standard magnesium sulfate solution. — The weighed pure magnesium sulfate heptahydrate was dissolved in distilled water and standardized by titration with standard EDTA solution, using Eriochrome black T as indicator. Concentration of the standard magnesium sulfate solution: 0.01131 mol./l.

0.5% *Eriochrome black T (E. B. T.) solution.*— A half gram of E. B. T. and 4.5 g. of hydroxylamine hydrochloride were dissolved in absolute ethanol and the total volume was filled up to 100 ml. with ethanol.

Buffer solution. — Ammonium chloride-ammonium hydroxide buffer was used. Each equivalent quantity of 1 mol. ammonium chloride solution and 1 mol. ammonium hydroxide solution were mixed.

Rare earth chlorides were prepared from the pure rare earth oxides which were all of extra pure grade, specially purified with ion-exchange resins. La_2O_3: more than 99.99%, CeO_2: more than 99.99%, Pr_6O_{11}: more than 99.99%, Nd_2O_3: more than 99.99%, Sm_2O_3: 99.98%.

All other reagents were of analytical reagent grade.

Apparatus.—Two or five ml. microburette (corrected) was used. One drop was equal to 0.005 or 0.006 ml. Micro glass filters (No. 4) and beakers were all boiled in 2% alkaline EDTA solution for about three hours and allowed to stand overnight and washed with distilled water thoroughly before use. The measurements of pH were carried out with the glass electrode pH meter EHM-1 Type of Hitachi & Co.

A sample solution, containing 1 to 5 mg. of the rare earth ion, was taken, the crystalline rare earth oxalate was precipitated, filtered and separated. An excess of the standard EDTA

1) G. Schwarzenbach, "Die Komplexometrische Titration", Ferdinand Enke Verlag, Stuttgart, (1955), p. 61.
2) H. Flaschka, *Mikrochim. Acta*, **1955**, 55.
3) G. Brunisholz and R. Cohen, *Helv. Chim. Acta*, **39**, 324 (1956); ibid., **39**, 2136 (1956).
4) J. K. Marsh, *J. Chem. Soc.*, **1950**, 1819.

solution was added and then the solution was made alkaline with dilute aqueous ammonia. The oxalate was completely dissolved as the rare earth-EDTA-oxalate complex anion[4]. By back titration of the excess of EDTA in the solution with standard magnesium sulfate solution, the rare earth was determined indirectly. The basis of calculation is derived from the fact that the rare earth-EDTA-oxalate complex is known as the 1 : 1 complex[4], which contains one gram atom of rare earth and one molecule of EDTA.

Results and Discussion

Back Titration in the Presence of Oxalate Ion.—Rare earth oxalate was dissolved as the complex anion with an excess of EDTA (HY^{3-}) in the solution and this reaction is supposed to proceed as follows: that is,

$$R_2(C_2O_4)_3 + 2HY^{3-} \rightarrow 2[RHYC_2O_4]^{2-} + C_2O_4^{2-}$$

in alkaline solution, where R^{3+} indicates the tripositive rare earth ion. When the excess of EDTA in the presence of the rare earth complex ion was back titrated with standard magnesium sulfate solution, using Eriochrome black T as indicator, the interference of the oxalate ion in solution was studied. To the aqueous solution of lanthanum or cerium chloride (content of rare earth ion: 2~4 mg.), about 10 to 70 mg. of oxalic acid was added and the crystalline rare earth oxalate was precipitated. Then an excess of standard EDTA solution was added and the solution was made alkaline with dilute ammonia water solution to dissolve the oxalate completely. After the pH was accurately adjusted to 10.0~10.5 with dilute ammonia water, 5 drops of 0.5% Eriochrome black T solution were added and the excess of EDTA remaining in solution was back titrated with standard magnesium sulfate solution till the blue color of the solution changed into red at the end point. The results are shown in Table I.

It had been supposed that the great excess of the oxalate ions would cause the end point of back titration to be ambiguous. But for 1 to 5 mg. of the rare earth ion, it was found that the addition of 30 mg. of oxalic acid did not interfere with the titration at all. Therefore, provided that the rare earth oxalate can be precipitated, separated and dissolved completely with a known amount of standard EDTA solution, the back titration of the excess of EDTA with standard magnesium sulfate solution is readily carried out in the presence of the oxalate ions and the rare earth-EDTA-oxalate complex ions in solution.

Studies on Various Conditions for the Determination of the Rare Earth Element.—Further, the conditions for this procedure for the determination of the rare earth elements were studied concerning the following matters, i. e.,

a) The process for the precipitation of crystalline rare earth oxalate. The crystalline oxalate was precipitated from a solution of rare earth chloride.

b) The amount of EDTA added for the complete dissolution of the oxalate. The use of 5 ml. of 0.01 M standard EDTA solution was optimum.

c) The amount of the buffer solution added to the solution obtained. The use of 2 ml. of the buffer solution was optimum.

d) The temperature for dissolution of the oxalate with the EDTA solution. 50 to 60°C (5 min.) was the best temperature

TABLE I. EFFECT OF VARIATION IN AMOUNT OF OXALIC ACID ADDED ON THE BACK TITRATION

Lanthanum taken=2.333 mg. pH=10.2~10.5

Oxalic acid added, mg.	La found, mg.	Error, mg.	%	Remarks
10	2.325	−0.008	−0.34	end point sharp
15	2.333	±0.000	±0.00	〃
20	2.333	±0.000	±0.00	〃
30	2.325	−0.008	−0.34	〃
40	2.317	−0.016	−0.69	lacks sharpness
50	2.317	−0.016	−0.69	〃
70	2.270	−0.063	−2.70	obscure

Cerium taken=3.595 mg. pH=10.2

Oxalic acid added, mg.	Ce found, mg.	Error, mg.	%	Remarks
20	3.586	−0.009	−0.25	end point sharp
30	3.576	−0.019	−0.53	〃
40	3.567	−0.028	−0.78	lacks sharpness

for the complete dissolution.

e) Adjustment of the pH for micro titration. The pH 10.2~10.5 was the optimum value which must be accurately kept.

f) On the indication of accurate end point of the back titration with standard magnesium sulfate solution in the presence of oxalate ion, using Eriochrome black T as indicator. The end point was defined to be accurately at the point where the blue color changed completely into the red color.

As the result of these experiments, the optimum conditions are found as follows.

Recommended Procedure.—1) *Precipitation and filtration of the crystalline rare earth oxalate.*— 10 ml. of a weak acid aqueous solution of the tripositive rare earth elements (content of R^{3+} ion: 1~5 mg.) is warmed at 60°C for a few minutes and 20 ml. of the saturated oxalic acid solution is added. The solution is warmed at the same temperature for several hours and then left to stand overnight. Large crystals of the rare earth oxalate are completely precipitated. The precipitate is filtered slowly with the micro glass filter (No. 4) by suction and washed with a saturated oxalic acid solution.

2) *Dissolution of crystalline rare earth oxalate.*—The precipitate is put into a small beaker together with the glass filter, about 25 ml. of distilled water is added and the mixture is warmed at 50~60°C for a few minutes. Then an excess of 0.01 M standard EDTA solution and 2 ml. of 2 N ammonia water are added and the mixed solution is warmed again carefully at 50~60°C for about 5 minutes. The precipitate is thus completely dissolved by this process. After complete dissolution of the precipitate, the solution is cooled rapidly and the glass filter is removed by washing with the distilled water which is added to the original solution.

3) *Back titration with standard magnesium sulfate solution.*—The pH of the solution obtained, must be correctly adjusted to 10.5 with 2 ml. of the buffer solution and dilute ammonia water. Then the total volume of the solution is filled up to about 60 ml. with distilled water. As this indicator, 5 drops of 0.5% E. B. T solution are added and the excess of EDTA in the solution is back titrated with 0.01 M standard magnesium sulfate solution. At the end point, the blue color changes completely into red.

The results obtained by this procedure are given in Table II.

TABLE II. MICROTITRATION OF SOME RARE EARTH ELEMENT

Element	Taken mg.	Found mg.	Error mg.
La	0.935	0.914	−0.021
	2.332	2.332	±0.000
	4.688	4.704	+0.016
Ce	1.798	1.815	+0.017
	3.595	3.605	+0.010
	5.393	5.322	−0.011
Pr	2.582	2.557	−0.025
Nd	1.617	1.627	+0.010
Sm	1.140	1.167	+0.027

It is especially necessary to notice the following matters in this procedure.

a) Determination of the tetrapositive cerium. In the complexometric titration of cerium in alkaline solution, to prevent the oxidation by the tetrapositive ion, it is necessary, in general, to add a reducing agent (e. g., one such as ascorbic acid), but in the presence of the oxalate ion, owing to its reducing property, addition of the reducing agent was not required and the procedure could be applied also to the determination of the tetrapositive cerium ion.

b) Addition of ethanol to the solution for back titration. Wünsch[5] added ethanol for the determination of scandium by complexometric back titration. Generally, in the case of the usual back titration for the determination of rare earth ions, addition of ethanol makes the end point evidently clearer with E. B. T as indicator, but in the presence of the oxalate ion, on the contrary, low value was obtained by adding ethanol.

c) Treatment of the glass vessels with alkaline EDTA solution. As Flaschka and Amin[6] reported, it was seen that the glass vessels were attacked slightly by concentrated EDTA solution and if so, there must be a tendency that a slightly high value for the determination would be obtained. Therefore, the glass vessels which were used in this experiment, were boiled with 2 percent alkaline EDTA solution and left to stand overnight and washed thoroughly with distilled water before use. In this way, such errors, owing to EDTA, were not recognized at

5) L. Wünsch, *Collection Czechoslov. Chem. Communs.*, **20**, 1107 (1955).
6) H. Flashka and A. M. Amin, *Mikrochim. Acta*, **1953**, 410.

all and the value found was accurate and reproducible.

This procedure of complexometric titration to determine the small amount of the rare earth from the oxalate is rapid and precise and more excellent than the usual gravimetric method in its accuracy.

Summary

The processes for dissolution of the oxalate and complexometry to determine the small amounts of rare earth rapidly and accurately, were studied. Crystalline rare earth oxalate was precipitated and filtered. The precipitate was dissolved completely with EDTA in alkaline solution and the excess of EDTA in solution was back titrated with standard magnesium sulfate solution. By this procedure, rare earth in the range of a content about 1 to 5 mg., was determined rapidly with a good accuracy.

The authors desire to thank the Ministry of Education for its financial support of this research.

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SHORT COMMUNICATIONS

Anion Exchange Studies of Beryllium(II), Cerium(IV), Thorium(IV) and Uranium(VI) Carbonate Complex Ions

By Seizo Misumi
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(Received December 10, 1958)

Ishimori and Okuno[1] studied anion exchange behavior of uranyl carbonate complex ion in a sodium carbonate solution and Saito and Sekine[2] reported that of thorium carbonate complex ion. No investigation has been reported on the behavior of beryllium and cerium(IV) carbonate complex ions toward anion exchange resins. In this paper, anion exchange behavior of macro amounts of beryllium, cerium, thorium and uranyl carbonate ions formed in ammonium carbonate solution and of tracer amounts of cerium and thorium carbonate complex ions formed in potassium carbonate were studied, using the "Dowex 1, X-8" anion exchanger (50~100 mesh) of carbonate form.

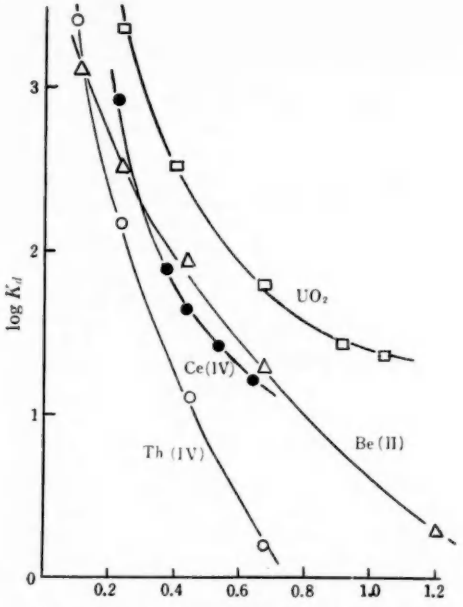
1) T. Ishimori and H. Okuno, This Bulletin, **29**, 78 (1956).
2) N. Saito and T. Sekine, ibid, **30**, 561 (1957).

The measurements of distribution coefficients were carried out as follows: one gram of the resin was added to 200 ml. of a series of ammonium carbonate solution of various concentrations containing an equal amount of beryllium carbonate complex ions. The solution was stirred frequently by a magnetic stirrer, allowed to stand for 12 to 20 hr. at about 20°C and the resin was rapidly separated from the solution with a glass filter. The metal ion in the resin was eluted by dilute hydrochloric acid and determined gravimetrically. The distribution coefficient K_d is given by:

$$K_d = [M_r] / [M_s] \quad (\text{ml./g.}) \qquad (1)$$

where M_r is the amount of metal ion in 1 g. of the resin and M_s is that in 1 ml. of the solution. The similar procedure was also applied to the cases of cerium, thorium and uranyl carbonate complex ions. The results are shown in Fig. 1.

It can be seen that beryllium and cerium ions formed the negatively-charged complex ions with ammonium carbonate in the similar manner to thorium and uranyl ions, and that the adsorbabilities of these metal carbonate complex ions decreased as the concentration of ammonium carbonate increased. It is expected from the difference of the values for K_d that



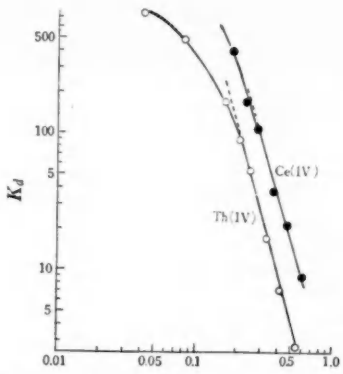
Concentration of ammonium carbonate (M)

Fig. 1. Distribution coefficients of beryllium, cerium, thorium and uranyl ions on anion exchanger in ammonium carbonate solution.
Amounts taken,
Be^{2+}: 11.7 mg (BeO)
Ce^{4+}: 7.3 mg (CeO_2)
Th^{4+}: 26.9 mg (ThO_2)
UO_2^{2+}: 61.0 mg (U_3O_8)

thorium ions can be effectively separated from uranyl ions with the ammonium carbonate solution.

The anion exchanger was saturated with beryllium carbonate complex ions in 0.1 M ammonium carbonate solution, and then washed with dilute ammonium carbonate solution. The results obtained for the exchange capacity by this measurement showed that one mole of beryllium ion corresponds to 1.97 ($\simeq$2.0) equivalents of the resin. This may indicate that the complex anion has a formula such as $[Be(CO_3)_2]^{2-}$ in 0.1 M ammonium carbonate solution.

Distribution coefficients of thorium-234 and cerium-144 in potassium carbonate solutions were determined by a similar procedure. Thorium or cerium in the resin was eluted with hydrochloric acid and the effluent was evaporated on a water bath. The measurements of radioactivities were carried out with a G-M tube. $\log K_d - \log(CO_3^{2-})$ curves plotted in



Concentration of potassium carbonate (M)

Fig. 2. Distribution coefficient of cerium-144 and thorium-234 on anion exchanger in potassium carbonate solution.

Fig. 2 show linearity for both elements from 0.25 to 0.60 M potassium carbonate solution. When only one species of negatively charged complex ion is assumed to be formed between a quadrivalent metal ion (M^{4+}) and carbonate ions, the main reaction would be

$$M^{4+} + xCO_3^{2-} = M(CO_3)_x^{4-2x} \quad (2)$$

$$K_1 = \frac{(M(CO_3)_x^{4-2x})}{(M^{4+})(CO_3^{2-})^x} \quad (2a)$$

Then the following equation is given as to the adsorption of the complex ion on the resin (R_2CO_3).

$$M(CO_3)_x^{4-2x} + (y/2)R_2CO_3 = R_yM(CO_3)_x + (y/2)CO_3^{2-} \quad (3)$$

$$K_2 = \frac{(R_yM(CO_3)_x)(CO_3^{2-})^{y/2}}{(R_2CO_3)^{y/2}(M(CO_3)_x^{4-2x})} \quad (3a)$$

Since the amount of M^{4+} is negligible compared with the amounts of "R_2CO_3", the latter can be regarded as a constant in the above equations. If the concentrations are replaced by thermodynamic activities, Eq. 1 is expressed as follows:

$$K_d = \frac{[M_r]}{[M_s]} = \frac{[R_yM(CO_3)_x]}{[M^{4+}] + [M(CO_3)_x^{4-2x}]} \quad (4)$$

In Eq. 3, y should be equal to $2x-4$ in order to preserve electrical neutrality in the resin. From Eqs. 2a, 3a and 4, the following equation is obtained:

$$\frac{d \log K_d}{d \log(CO_3^{2-})} = 2 - x \quad (5)$$

Since the slopes in Fig. 2 are numerically correspond to $-3.9 \sim -3.8$, the charges of

thorium and cerium(IV) carbonate complex ions could be −8 (their some portions seem to have other values, e.g., −6) in the range between 0.25 and 0.60 M potassium carbonate solutions on the basis of the assumption described above. However, it is probable that these carbonate complex ions include OH^- radicals. Further, it is also supposed that more than one species of negatively charged complex ions may exist and be adsorbed on the resin in other ranges of concentrations of potassium carbonate solutions.

Details of these results will be published elsewhere.

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The Separation of Thorium(IV) and Cerium(III) Ions by Using Alginate as Cation Exchanger

By Takeo Takahashi and Shingo Miyake

(Received April 3, 1959)

Recently the separation of thorium(IV) and cerium(III) ions by the use of strongly acidic cation exchange resins, such as Dowex 50 or Amberlite IR-120 has been reported by a few workers[1-4].

The present authors will report here a new method for the separation of thorium (IV) and cerium(III) by using alginate as ion exchanger and dilute nitric acid as eluant.

Alginic acid, a natural polyacid, has a property of cation exchanger for several metallic ions in a moderately acid solution of pH 1~3. Metallic ions adsorbed on alginic acid can be eluted easily and separately with dilute acid solutions of varying concentration.

Preparation of Alginate Exchanger and Column.—The alginate exchanger was prepared by swelling the thread* of calcium alginate in a dilute sodium hydroxide solution (less than 0.1 N) for about 30 min. and then by immersing in 0.5 N nitric acid. The product was packed appropriately into a glass tube (1.5 cm. in diameter, 30 cm. in length). The column packed with the adsorption bed of alginate (length, about 20 cm.) was washed successively with 250 ml. each of 0.5 N nitric acid and distilled water. Thus, the alginate was converted completely into acid form.

Procedure.—The mixed solution of thorium(IV) and cerium(III) ions was poured onto the column, the pH being adjusted to 2~2.5 with aqueous ammonia. The bed was then washed with 100 ml. of distilled water, and 200 ml. of 0.075 N nitric acid was passed through the column at a flow rate of about 1 ml./min. By this treatment, all the cerium(III) ions were completely eluted, and then all the thorium-(IV) ions remaining on the column were eluted in the same manner with 100 ml. of 1 N nitric acid.

The amount of throium(IV) and cerium-(III) ions in the effluents was colorimetrically determined with Neo-thoron for thorium(IV) (580 mμ)[5] and with hydrogen peroxide for cerium(III) (320 mμ)[6].

Result.—An example of elution diagrams of the solution containing 35.5 mg. of thorium(IV) and 30 mg. of cerium(III) ions is shown in Fig. 1, and the amounts initially taken are given in Table I in comparison with the amount finally found.

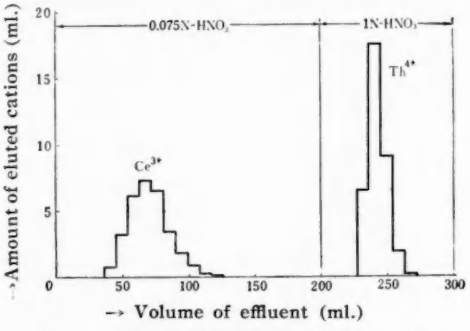

Fig. 1. The elution diagram in the separation of thorium(IV) and cerium(III). The eluants were 0.075 N nitric acid for cerium and 1 N for thorium.

1) L. Gordon et al., *Anal. Chem.*, **28**, 1476 (1956).
2) T. Taketatsu, This Bulletin, **32**, 291 (1959).
3) T. Nishi et al., *III Atomic Energy Symposium (Abstr.), Japan*, 69 (1959). Japan Scientific Council, Tokyo.
4) T. Nozaki, *J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zasshi)*, **76**, 996 (1955).

* The alginate thread was supplied from Kamogawa Kako Co., Ltd., to whom the authors are indebted to appreciate.

5) Y. Ishibashi and S. Higashi, *Japan Analyst*, **4**, 14 (1955).
6) M. Malinek and L. Klir, *Chem. Abstr.*, **50**, 13659*a* (1956).

TABLE I. ANALYTICAL RESULT (CALCULATED FROM FIG. 1)

	Taken (mg.)	Found (mg.)	Error (mg.)
Th(IV)	35.5	35.4	0.1
Ce(III)	30·0	30.3	0.3

It would be concluded that the new method with alginate as ion exchanger has an advantage as an industrial and an analytical method for the separation of thorium(IV) and cerium(III).

The authors are grateful for the Grant from the Ministry of Education.

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Decomposition of Solid Ammonium Nitrate by γ-Ray

By Toshiaki SHIRAI
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(Received May 8, 1959)

When irradiated with ultraviolet light or ionizing radiation, solid metal nitrates are reported to decompose, producing nitrite and oxygen[1]. However, no investigation has been reported on the decomposition of ammonium nitrate. Recently, the authors carried out the irradiation of ammonium nitrate by γ-ray from 1000 Curie ^{60}Co source at the Institute of Physical and Chemical Research. Decomposition products in gaseous phase were analyzed by a mass spectrometer of CEC 21-103A type and the effect of salt addition on the rate of decomposition was studied.

The irradiation of the salt was carried out in vacuo at a dose rate of 4.4×10^5 r/h, at 23°C. The irradiated sample was washed into a clean beaker with CO_2 free water and the resulting solution was titrated for ammonium ion by the method of Marcali and Rieman[2].

On dissolving the irradiated salt in water, copious effervescence occurred, similar phenomenon was reported for some metal nitrates[1b,c,d].

TABLE I. DECOMPOSITION OF AMMONIUM NITRATE BY γ-RAY

Total dose (10^7r)		4.2	7.1	10.5	15.6
W/W_0*		0.99	0.98	0.97	0.97
Total dose (10^7r)		4.1	6.9	11.1	
	Salt** added				
W/W_0*	$LiNO_3$	0.98	0.97	0.98	
	$NaNO_3$	0.98	0.98	0.97	
	KNO_3	0.98	0.97	0.96	

* W: Mass of ammonium nitrate present
W_0: Initial mass of ammonium nitrate
** Concentration, 5 mol. %

In some case, the solution was divided into two parts, one was titrated for the ammonium ion and the other for the nitrate ion with sodium hydroxide after conversion of ammonium nitrate into nitric acid by passing H-form cation exchanger. The amount of NO_3^- was exactly equivalent to that of NH_4^+ plus added metal ion. NO_2^- was not detected, with the method of Griess[3], in contrast to the case of metal nitrates. Table I shows that the decomposition is accelerated by the addition of metal ion. At this stage, however, no definite conclusion may be drawn in this connection, as decomposition was not carried far enough to show the effect clearly.

Following peaks were found in the mass spectrogram of decomposition products in gaseous phase; 14, 16, 17, 18, 28, 29, 30, 32, 44 and by m/e. Main peaks were 18, 28, 30 and 44 by m/e and they are assigned to be H_2O, N_2, NO, and N_2O, respectively. This feature is qualitatively the same as that obtained for the thermal decomposition of the salt[4]. The effervescence is ascribed to the gas captured in the solid. The quantitative analysis is now being done. This, together with a detailed discussion of the above results, will be reported elsewhere.

The authors wish to thank Dr. N. Matsuura for the valuable discussion and Mr. M. Takizawa in charge of operating the radiation source at the Institute of Physical and Chemical Research.

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1) a. L. Narayanswamy, *Trans. Faraday Soc.*, **31**, 1411 (1935).
b. A. Allen and J. Ghormley, *J. Chem. Phys.*, **15**, 208 (1947).
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Cyclooctatetraene Iron Tricarbonyl

By Akira Nakamura and Nobue Hagihara

(Received May 8, 1959)

Recently Hallam and Pauson[1] investigated butadiene iron tricarbonyl and its derivatives and concluded that the conjugation of the double bonds was essential for the formation of such compounds. However, Pettit[2] reported the preparation of analogous compounds with non-conjugated bicyclo [2.2.1] heptadiene. He considered that a suitable spatial arrangement of the double bonds, not their conjugation was necessary for their effective overlap with the atomic orbitals of the metal which was an essential factor leading to the bond formation.

Since cyclooctatetraene(COT), in its tub form, seems to have such a suitable spatial arrangement of the double bonds, we have tried to prepare cyclooctatetraene iron tricarbonyl, $(C_8H_8)Fe(CO)_3$ (I), and its successful preparation is reported here*.

After irradiation of an equimolar mixture of COT and iron pentacarbonyl with sunlight for 8 hr. and subsequent removal of the unreacted starting materials under reduced pressure, dark red crystals were obtained in 10% yield. These crystals were purified by sublimation under reduced pressure (5 mmHg) at 80°C or by recrystallization from light petroleum.

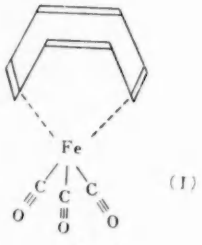
Anal. Found: C, 54.31; H, 3.35; mol. wt. (Rast), 243. Calcd. for $C_{11}H_8FeO_3$: C, 54.14; H, 3.31%; mol. wt., 244.

The combustion analysis apparently conformed to the composition, $(CO)_3Fe.(C_8H_8)$ (I). The purified compound I was beautiful dark red needles, melting at 94°C without decomposition and was stable in air and readily soluble in most organic solvents including pyridine and glacial acetic acid. I dissolved in cold concentrated sulfuric acid and could be recovered unchanged on neutralization, but it decomposed when its solution in concentrated sulfuric acid was heated to 110°C. The solution of I in carbon tetrachloride reacted readily with bromine at room temperature to give ferric bromide and brominated products of COT. I could also be prepared by heating the both components under nitrogen at 120°C for 18 hr.

The infrared spectrum of I (in KBr disk) showed bands at 1961 and 2050 cm^{-1} and at 699, 716 and 720 cm^{-1}. The former group of bands is similar to those of butadiene iron tricarbonyl and the latter group of bands indicates the presence of *cis*-type double bonds.

In the visible region of the spectrum no distinct absorption maxima were observed. In the ultraviolet region it showed a weak absorption maximum at 300 mμ ($\log \varepsilon$: 3.99 in 95% alcohol) similar to that of COT. On treatment with aqueous potassium iodide-iodine solution at 50°C, the solution of I in benzene evolved 3 mol. of carbon monoxide indicating the presence of three $-C\equiv O$ groups in one molecule of I. For further proof of the structure of I, I was decomposed by iodine in toluene. COT was detected in the decomposition products by its reaction with mercuric sulfate to give phenyl acetaldehyde. COT formed was further identified and determined by gas chromatography (the yield of COT was 76%).

From the above results it may be concluded that COT is π-bonded to iron without change in its skeletal structure. It is a well established fact that the molecule of COT is not planar. Therefore, it may be reasonable to assume that COT molecule in I would not be planar, too; and the following structure of I is proposed:



(I)

Fig. 1

When iron pentacarbonyl was used in excess in the photosynthesis of I, yellow crystals were obtained in addtion to I in 3% yield from COT. These crystals were purified by fractional sublimation at 120°C (5 mmHg) followed by recrystallization

1) B. F. Hallam and P. L. Pauson, *J. Chem. Soc.*, **1958**, 642.

2) R. Pettit, *J. Am. Chem. Soc.*, **81**, 1266 (1959).

* After completion of our work, it has become known to us that T. A. Manuel and F. G. A Stone, (*Proc. Chem. Soc.*, **1959**, 90), also reported the preparation of cyclooctatetraene iron tricarbonyl and the related compounds. They suggested a planar structure to COT which was attached to the iron atom of cyclooctatetraene iron tricarbonyl. In their report, however, no practical description of the preparation of these compounds are given.

from benzene to give orange-yellow needles which decomposed at 185°C.

Anal. Found: C, 43.72; H, 2.35. Calcd. for $C_{14}H_8FeO_6$: C, 43.80; H, 2.11%.

The combustion analysis conformed to the composition, $(CO)_3Fe(C_8H_8)Fe(CO)_3$ (II). This compound II was slightly soluble in light petroleum and methanol, soluble in pyridine, glacial acetic acid and benzene, insoluble in hydrochloric acid and aqueous sodium hydroxide solution. It decomposed in concentrated sulfuric acid at room temperature.

(II)

Fig. 2

The infrared spectrum of II (in KBr disk) showed bands at 1972 and 2035 cm^{-1} for CO stretching region. The characterictic bands indicating the presence of *cis*-type double bonds which were shown in the infrared spectrum of I did not appeared and the whole spectrum was relatively simple compared with that of I, suggesting the higher symmetry of the molecule of II. The ultraviolet absorption spectrum of II had a shoulder at 258 mμ ($\log \varepsilon$: 3.15, in 95% ethanol) and no distinct absorption bands appeared in the visible region. Compared with the absorption band of I the shift of the band toward shorter wavelength and the decrease in intensity are apparent. These spectral changes in the ultraviolet region may be considered to indicate the immobility of the π-electrons of COT in II. From the above results the structure shown in Fig. 2 is proposed.

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On the Preparation of Isotopically Pure Light Hydrogen

By Koshiro Miyahara and Takao Kwan

(Received June 8, 1959)

Natural abundance of heavy hydrogen isotope in the water is known to vary depending on the geochemical circumstances in which the water is found[1]. The standardization of the value of D-content in the water or the preparation of isotopically pure light hydrogen was thus needed and became the object of careful investigation particularly by Titani and his co-workers[2,3]. Electrolysis of water is known to produce hydrogen of less D-content. Combustion of the hydrogen followed by re-electrolysis leads to much less concentration in the heavy component. Repeating such procedure, these authors were able to obtain 125 g. light water, the atomic D% of which being 0.0002±20%, i.e., about one-hundredth of natural abundance.

Current investigation on the chromatography, on the other hand, showed that this technique is powerful for the separation of hydrogen isotopes. Glueckauf and Kitt[4] were able to isolate pure deuterium (99.5%) by a displacement technique using palladium as column packing. The work[5] of this laboratory proved that hydrogen isotopes are separated in the elution chromatogram when synthetic zeolite (Linde molecular sieve) is used as column packing and kept at −195°C.

Deuterium was found to adsorb strongly compared with ordinary hydrogen on this packing. As a result, self-displacement of a mixture of hydrogen isotopes through such a cooled column yielded pure hydrogen in the frontal band and then HD and D_2 in the succeeding band[5]. The detection of hydrogen isotopes were made in this case by the thermal conductivity gauge equipped in Shimadzu Gas Chromatograph GC 1A.

1) M. Harada and T. Titani, This Bulletin, **10**, 206, 263 (1935); G. R. Clarke, *Nature*, **174**, 469 (1954).
2) T. Titani, S. Horibe and M. Kobayakawa, *Mass Spectroscopy*, **9**, 32 (1957).
3) T. Titani, S. Horibe, T. Komori and M. Kobayakawa, ibid., **9**, 40 (1957).
4) E. Glueckauf and G. P. Kitt, "Vapour Phase Chromatography", Butterworths Scientific Publications, London, (1957), p. 422.
5) S. Ohkoshi, Y. Fujita and T. Kwan, This Bulletin, **31**, 771 (1958).

It is obvious that the latter technique is promising to obtain isotopically pure light hydrogen. An attempt was made therefore to investigate the isolation of light component from ordinary hydrogen by means of such chromatographic technique. A spiral Pyrex column 400 cm. long and 0.5 diameter was filled with molecular sieve 5A and degassed overnight at 300°C by mercury diffusion pump. Two liters hydrogen sample from commercial electrolytic hydrogen* was introduced into the one side of the column immersed in liquid nitrogen. About ten minutes later hydrogen was found to appear on the other side of the column. The initial portion of the hydrogen (100~200 cc. N. T. P.) was then collected in a flask (sample I). The remaining hydrogen, together with those adsorbed on the packing, were collected back to the original flask (sample II). The deuterium content of the two samples were analyzed by Hitachi Mass Spectrometer RMD-3. The result is shown in Table I.

TABLE I

Run	Hydrogen sample	Volume cc. N.T.P.	Atomic D%	Error
1	I	100	0.0000	±0.0005
	II	1900	0.0068	
2	I	200	0.0004	±0.0005
	II	1800	0.0068	

As shown in this table, the sample I was found almost perfectly free from heavy component within the accuracy of the mass spectrometer. Thus, it is quite evident that the chromatographic process is simple and efficient to prepare isotopically pure light hydrogen. At the same time, the process is of practical importance to enrich deuterium or tritium at least in laboratory scale[5].

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* Supplied by Hokkaido Soda Co., Horobetu.

Photosensitized Oxidation of Isopropylalcohol in the Presence of Zinc Oxide

By Isao KOMURO, Yuzaburo FUJITA and Takao KWAN

(Received June 8, 1959)

As reported previously[1], two of us (Y.F. and T.K.) found that photodesorption of oxygen takes place on reduced zinc oxide whereas it turns to irreversible sorption on oxidized sample. This opposite fashion of the photoresponse in the adsorption of oxygen stimulated us to investigate how these phenomena should be associated with the photosensitized oxidation reaction[2] known to occur on zinc oxide. Experiments were made, therefore, along with this interest.

The oxidation of isopropylalcohol by oxygen in liquid phase was chosen for the purpose. Commercial zinc oxide powder (guaranteed reagent) supplied by KANTO KAGAKU was outgassed at 480°C for one hour in vacuo. On cooling it was poured into isopropylalcohol. This zinc oxide sample is called here as reduced zinc oxide. On the other hand, the commercial zinc oxide was used without any special pretreatment. The sample is supposed to be in oxidized state, since the d.c. electrical resistance measurement has shown that it possesses a resistance value as large as that of oxidized zinc oxide or is much larger than that of reduced zinc oxide.

A 50 ml. dried isopropylalcohol containing 2 g. reduced or oxidized zinc oxide was put into a round Pyrex flask having three openings, two of which being for thermometer and mercury manometer respectively and the remaining being connected to a reflux condenser and then to a gas burette.

Oxygen was introduced from the gas burette into the flask immersed in 65°C thermostat. The oxidation reaction was allowed to proceed with stirring reactant phase operated by magnetic rod placed in the flask. The apparatus was isolated when working. The rate of oxidation was followed by recording the decrease in the gas volume of the burette at a constant

1) Y. Fujita and T. Kwan, This Bulletin, **31**, 380 (1958).
2) For example, see M.C. Markham and K. J. Laidler, *J. Phys. Chem.*, **57**, 363 (1953).

pressure. The partial pressure of oxygen inside the flask was estimated to be 440 mmHg during the reaction.

Irradiation of light was made by Matuda Mercury Lamp SHL 100 UV without filter of any kind but through the window of the thermostat. The reaction product was pipetted and subjected to gas chromatographic and chemical analyses after the measurement of the oxidation rate. The temperature of the oxidation reaction was determined by the thermometer immersed directly in the liquid phase of the reacting system. Illumination caused the temperature of the system to rise less than 2°C.

It was confirmed that without illumination little consumption of oxygen occurs on reduced zinc oxide kept at 65°C. Illumination, however, brought forth distinct consumption of oxygen. On intercepting the light, the consumption occurring steadily was found to cease apparently. Reillumination caused consumption of oxygen again to proceed, so that the photocatalytic oxidation of isopropylalcohol was almost reversible with respect to on or off of the light switch.

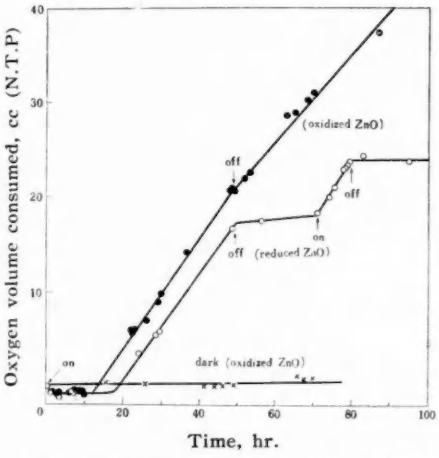

Fig. 1. Oxidation of isopropylalcohol by oxygen on zinc oxide with or without illumination.
T: 65~67°C. P_{O_2}: 440 mmHg.

Now, in the case of oxidized zinc oxide, the photosensitized oxidation reaction took place quite similarly as the case on reduced zinc oxide, while the reaction did not proceed without illumination beyond the period of 70 hr. However, strikingly different behavior was that interception of light still perimits the oxidation reaction to proceed with a speed almost equal to that of illumination. All the rate data for the oxidation of isopropylalcohol are shown in Fig. 1. Gas chromatographic and chemical analyses indicated that the product contains nothing other than acetone and hydrogen peroxide. The oxidation reaction may hence be expressed by

$$\begin{matrix} CH_3\text{-}CH\text{-}CH_3 \\ \quad\quad | \\ \quad\quad OH \end{matrix} + O_2 = CH_3\text{-}CO\text{-}CH_3 + H_2O_2$$

As shown previously[1], adsorbed oxygen due to illumination was unable to desorb from the surface of oxidized zinc oxide on intercepting light whereas photodesorption was almost reversible on the surface of reduced zinc oxide. If it is accepted that the photoresponse of this kind should hold even during the oxdation reaction of isopropylalcohol, the different photocatalytic behavior shown above respectively on reduced and oxidized zinc oxide is to be anticipated. Because the catalyzing surface of reduced zinc oxide varies, when oxygen is present, depending on whether the light is switched on or off whereas the surface of oxidized zinc oxide, once experienced illumination, may maintain its state even during the light is intercepted.

On the other hand, almost identical photocatalytic activity shown by the two zinc oxide samples during the initial stage, including the induction period, and later is unexpected and rather embarrassing. Further work is in progress.

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*Syntheses of Kinetin-analogues. II**

By F. Shigeo Okumura, Yachio Kotani, Tomoyuki Ariga, Mitsuo Masumura and Susumu Kuraishi**

(Received June 8, 1959)

In the previous paper[1] the authors reported the relation between the chemical

* Presented at the 25th Anniversary Meeting of the Botanical Society of Japan, held at Tokyo in October, 1957.

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1) F. S. Okumura et al., This Bulletin, **30**, 194 (1957).

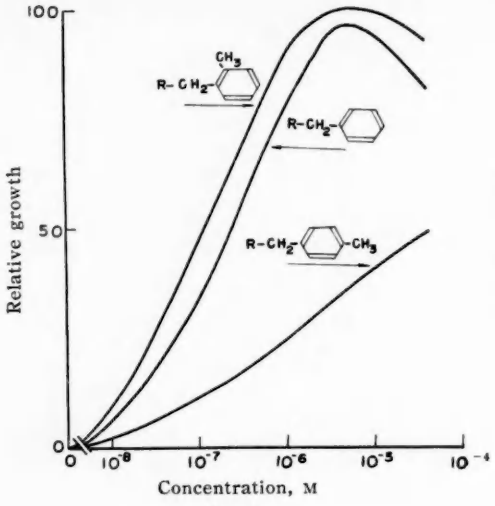

Fig. 1.
R=Aminopurine

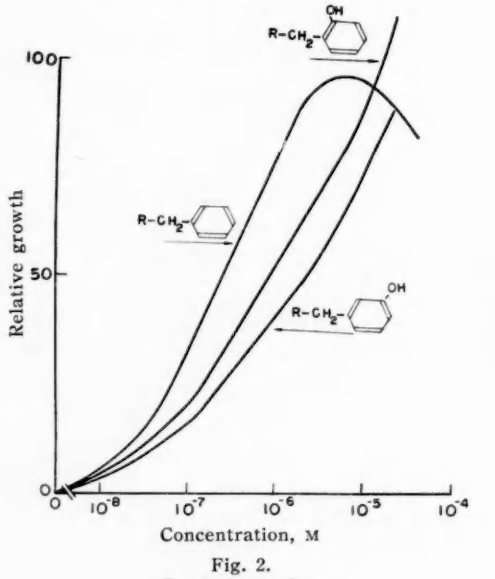

Fig. 2.
R=Aminopurine

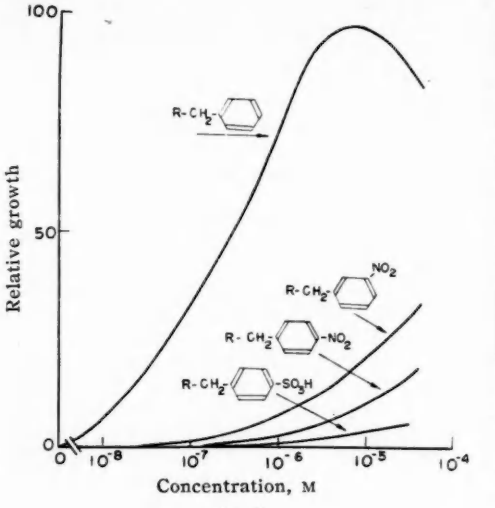

Fig. 3.
R=Aminopurine

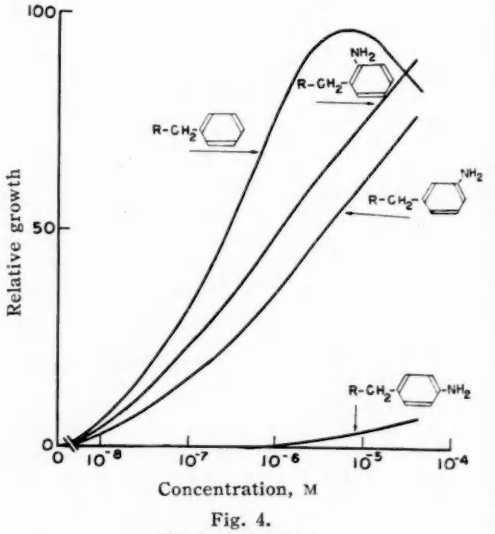

Fig. 4.
R=Aminopurine

structure and the physiological activity of kinetin-analogues by using the leaf test method[2] (*Raphanus sativus L. var. acanthiformis* Makino). It was shown[1] that the kinetin-analogues which have a benzene ring instead of a furan ring have almost the same activity as kinetin on leaf growth.

Seventeen kinetin analogues with various substituents in the benzene ring of 6-(benzylamino)-purine have been synthesized in order to investigate the effect of substituents on leaf growth. Positive and negative substituents, such as methyl, hydroxyl, methoxyl, amino, nitro and sulfonic acid groups were introduced into the ortho, meta or para position of the

2) S. Kuraishi and F. S. Okumura, *Bot. Mag., Tokyo*, **69**, 300 (1956).
3) M. W. Bullock, J. J. Hand and E. L. R. Stockstad, *J. Am. Chem. Soc.*, **78**, 3693 (1956).

TABLE I. SYNTHESES OF SUBSTITUTED 6-(BENZYLAMINO)-PURINES

Substituent	Temp. (°C) and time (hr.) of run		Yield (%)	m.p. (°C)	Analysis N%	
					Found	Calcd.
o-Methyl	130~140[a]	11	67.5	242[b],[e]	29.52	29.27
p-Methyl	130~140[a]	13	65.0	264[c],[e]	29.19	29.27
o-Amino	130~140	5	25.4	279~280[e]	34.81	34.98
m-Amino	120~130	4	49.3	243~244[e]	35.13	34.98
p-Amino	120~130	5	25.2	239~240[e]	35.19	34.98
m-Nitro	130~140	5	34.0	272[e]	31.06	31.15
p-Nitro	90	4	10.3	220~226[d],[e]	29.86	31.15
o-Hydroxy	135	4	23.2	264[h]	29.93	29.04
m-Hydroxy	140~150[a]	18	22.8	284~286[e]	29.20	29.04
m-Methoxy	130~135[a]	13	30.4	248~249[f]	27.46	27.44
o-Chloro	125~130[a]	11	60.8	227~228[e]	27.01	26.97
m-Chloro	130[a]	15	59.0	241~242[e]	26.92	26.97
p-Chloro	120[a]	17	70.5	280~280.5[e]	27.16	26.97
p-Sulfo	160~170	20	12.0	238~242[d],[g]	24.14	22.94

a) in a sealed tube b) 243~244°C[2] c) 263°C[3] d) This compound is still impure.
e) Ethanol f) Methanol g) Water h) Dimethylformamide

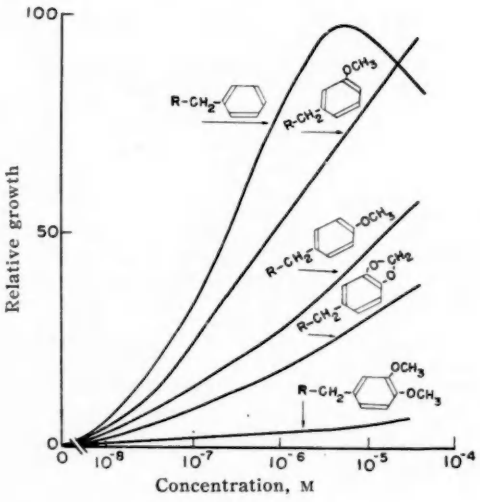

Fig. 5.
R=Aminopurine

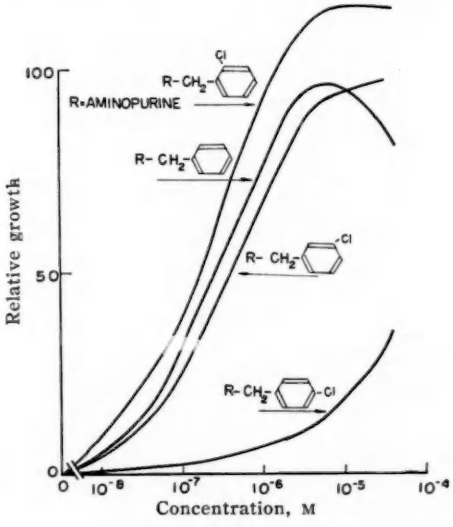

Fig. 6.
R=Aminopurine

benzene ring. In these seventeen analogues, fourteen are new compounds and three have already been reported[1].

The results are shown in Figs. 1, 2, 3, 4, 5 and 6. It is of interest that the ortho substituted isomers are the most active on leaf growth and the activity decreases in the order of the meta and the para isomers. Furthermore, it is noteworthy that the activity of some ortho isomers in higher concentration is stronger than that of 6-(benzylamino)-purine in its optimum concentration, e.g., *o*-methylbenzylaminopurine (Fig. 1), *o*-hydroxybenzylaminopurine (Fig. 2) and *o*-chlorobenzylaminopurine (Fig. 6) and that the kinetin activity is decreased by both meta and para substitution. It is clear from the above facts that the kinetin activity is favored by the ortho-substitution but disfavored by the meta- or para-substitution.

Experimental.—The syntheses of substituted 6-(benzylamino)-purines were achieved by condensing 6-(methylmercapto)purine with various amines. In general, 6-(methylmercapto)-purine was heated with 2 to 3 molecular equivalents of an amine with or without a solvent in a sealed or open tube at the given temperature and for the period given in Table I.

6-(*o*-Chlorobenzylamino)purine.—A mixture of 0.3 g. of 6-(methylmercapto)-purine (3.5 mol.) and 0.87 g. of *o*-chlorobenzylamine (1 mol.) was heated for eleven hours under reflux at 125~130°C. After cooling, the reaction product was precipitated by the addition of acetone, collected, washed with acetone, and then recrystallized from ethanol to give the product, m.p. 227~228°C, in a yield of 60.8%.

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*Syntheses of Kinetin-analogues. III**

By F. Shigeo Okumura, Noboru Enishi, Hiroyuki Itoh, Mitsuo Masumura and Susumu Kuraishi**

(Received June 8, 1959)

In the first paper of this series[1], the authors showed that 6-(*n*-hexylamino)-purine has almost the same activity on the growth of *Raphanus* leaf as kinetin, and the furan ring of kinetin can be replaced by an alkyl group without causing a remarkable decrease in the kinetin activity. It is very interesting to investigate the relation between the carbon

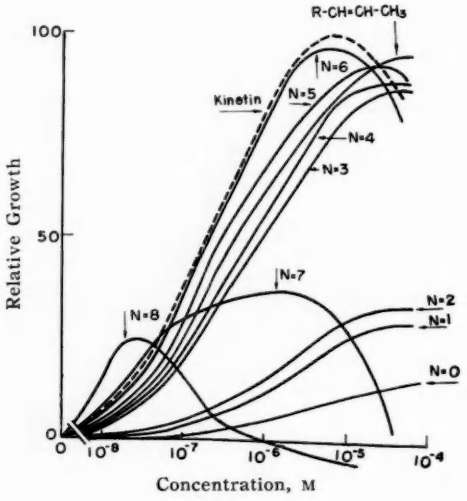

Fig. 1.
$R \cdot C_NH_{2N+1}$
N=0—8
R=Aminopurine

Table I. Syntheses of 6-(Alkylamino)-purines

Alkyl	Temp. (°C) and time (hr.)	of run	Yield (%)	m.p.	Analysis N% Found	Calcd.
Methyl	130~140	14[a]	74.0	308[b],[j]	46.96	47.00
Ethyl	130~135	17[a]	42.0	234~235[c],[j]	42.76	42.92
n-Propyl	130~140	20[a]	39.5	234[j]	38.59	39.52
Allyl	130~140	10	48.7	221~222[g]	39.60	39.96
n-Butyl	130	20[a]	36.0	228~229[d],[h]	36.58	36.63
n-Amyl	100	15	37.0	164~165[k]	34.21	34.12
n-Hexyl	130~135	9	31.0	177~178[h]	32.81	31.94
n-Heptyl	130~140	14	54.2	175~176[g]	30.00	30.02
n-Octyl	140~145	15[a]	53.0	168~170[j]	28.13	28.34
n-Nonyl	125~135	12	30.1	165~166[h]	26.12	26.79
Geranyl	100~115	8	21.0	146~148[i]	25.90	25.82
n-Dodecyl	150~160	16[a]	50.4	154~156[g]	23.68	23.08
n-Octadecyl	160~165	18[a]	51.0	153~154[g]	18.82	18.12
Dimethyl	130~135	17[a]	45.0	263~264[e],[j]	43.08	42.92
Diethyl	110	8[a]	51.4	217~219[f],[h]	36.70	36.65
Dibutyl	115~125	8[a]	24.8	124~125[h]	28.60	28.32

a) in a sealed tube b) m.p. 312~314°C[2] c) m.p. 238~239°C[2] d) m.p. 233~234°C[2] e) m.p. 251°C[2] f) m.p. 186°C[2] g) Ethanol h) Aq. ethanol i) Aq. methanol j) Water k) Benzene

* Presented at the 25th Anniversary Meeting of the Botanical Society of Japan, held in October, 1957.

** Biological Institute, College of General Education, The University of Tokyo, Meguro-ku, Tokyo.

1) F. S. Okumura et al., This Bulletin, **30**, 194 (1957).
2) G. B. Elison, E. Burgi and G. H. Hitching, *J. Am. Chem. Soc.*, **74**, 411 (1952).

number in the side chain of 6-(alkylamino)-purines and the leaf growth activity.

Sixteen 6-(alkylamino)-purines have been synthesized for this purpose, eleven of which are new compounds, and tested for their physiological activity on the growth of the leaf of *Raphanus sativus L. var. acanthiformis* Makino. The results are shown in Fig. 1.

The activity of the first three members with 0, 1 and 2 carbon atoms in the side chain is very weak, but a sudden increase of activity is observed in 6-(*n*-propylamino)-purine and then the activity gradually increases with the carbon number until the peak of activity is attained in 6-(*n*-hexylamino)-purine, and then the activity decreases rapidly in 6-(*n*-heptylamino)- and 6-(*n*-octylamino)-purines. No activity was observed with higher homologues with 9, 10, 12 and 18 carbon atoms in the side chain.

The activities of 6-(dialkylamino)-purines such as 6-(dimethylamino)-, 6-(diethylamino)- and 6-(dibutylamino)-purines were very weak.

Experimental.—6-(Alkylamino)-purines were prepared by the reaction of 6-(methylmercapto)-purine with aliphatic amines. In general, the 6-(methylmercapto)-purine was heated with an amine in a sealed or open tube without any solvent, but an aqueous solution was used in the case of the volatile amines. After cooling, the reaction product was either precipitated by the addition of acetone, or it was obtained as a residue after evaporation of the excess of the amine under reduced pressure. The product was then recrystallized from an appropriate solvent.

6-(*n*-Hexylamino)-purine. — A mixture of 1.00 g. (1 mol.) of 6-(methylmercapto)-purine and 1.8 g. of *n*-hexylamine (3 mol.) was heated in a sealed tube at 130~135°C for 9 hr. After cooling, the reaction mixture was evaporated to dryness and the residue was recrystallized from 60% ethanol (yield, 0.4 g. or 31.5%).

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The Rate of the Color Reaction of m-Dinitrobenzene with Sodium Hydroxide in Acetone

By Takehiro Abe

(Received July 6, 1959)

Investigations of kinetics of the color reactions producing Meisenheimer's intermediates[1] have been studied by Caldin, Long and Ainscough[2,3] on the coloration reactions between trinitrobenzenes and ethoxide ion, and also by Nagakura, Oosawa and Tsubomura[4] on the decoloration reaction of the color product between 2, 4-dinitroanisole and hydroxyl.

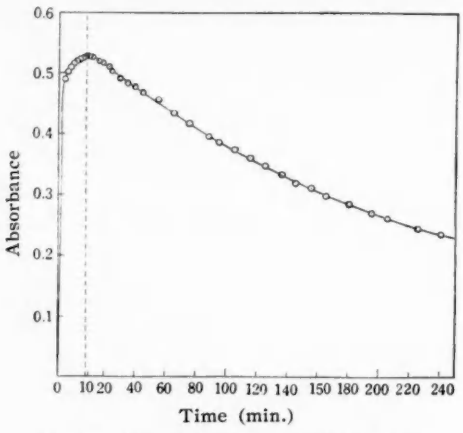
The author has succeeded in pursuing changes in absorbance of a visible absorption of a colored species through both coloration and decoloration reactions in a whole substitution reaction of *m*-dinitrobenzene with sodium hydroxide in acetone.

In the previous paper[5], the author has reported the visible absorption curve (530~600 mμ) of the colored solution produced by adding sodium hydroxide to *m*-dinitrobenzene in acetone. This color becomes more intense for several minutes and then fades slowly. The result in Fig. 1 was obtained by following the absorbance d of the 560 mμ absorption of the colored species at 25°C. The coloration and decoloration reactions are formulated provisionally as

$$m\text{-Dinitrobenzene} + \mathrm{NaOH} \xrightarrow{\text{Coloration}} [m\text{-Dinitrobenzene}\cdot\mathrm{OH}]^- \text{ Colored species (transition complex)} \xrightarrow{\text{Decoloration}} \text{A final product}$$

Although both the coloration and the decoloration are actually concurrent, we assume that only coloration reaction proceeds till nine minutes, at which time the maximum absorbance is obtained, and that only the decoloration occurs from that time,

1) J. Meisenheimer, *Ann.*, **323**, 214, 241 (1902).
2) E. F. Caldin and G. Long, *Proc. Roy. Soc.*, **A228**, 263 (1955).
3) J. B. Ainscough and E. F. Caldin, *J. Chem. Soc.*, **1956**, 2528.
4) S. Nagakura, S. Oosawa and H. Tsubomura, Presented at the Symposium on Electron States of Molecules at Kyoto in October, 1958.
5) T. Abe, This Bulletin, **32**, 775 (1959).
6) T. Abe, to be published in ibid., **32**, No. 9 (1959).



Flg. 1. Change in the absorbance of the 560 mμ absorption for the colored solution of *m*-dinitrobenzene (2.33×10^{-5} M) and sodium hydroxide (3.49×10^{-3} N) in acetone, at 25°C (path length of absorption cells, 1 cm.).

since the rate of the coloration reaction is much greater than that of the decoloration, as can be known from Fig. 1. Moreover, on an assumption that *m*-dinitrobenzene completely changes into the colored species just after nine minutes, a value of 2.27×10^4 can be obtained as a molar extinction coefficient ε of the 560 mμ absorption of the colored species. This value is of the same order, as compared with the molar extinction coefficients of the red complexes of trinitrobenzene and its derivatives with ammonium hydroxide[6]. From this it is, therefore, known that the above assumptions are very good. Under a condition that the concentration of sodium hydroxide is sufficiently larger than that of the colored species produced, the rate constant k_C of the coloration reaction of the second can be derived as follows:

$$k_C=\frac{1}{0.4343(C_{DNB}-C_{OH})(t-t_{0C})}\log\frac{C_{DNB}-d/\varepsilon}{C_{DNB}-d_{0C}/\varepsilon} \quad (1)$$

where C_{DNB} is the initial concentration of *m*-dinitrobenzene, C_{OH}, the initial concentration of sodium hydroxide, d, the absorbance of the colored species after t minutes, and d_{0C}, the value of d after arbitrary t_{0C} minutes. On the other hand, the following empirical formula of the first order satisfactorily represents the observed rate constants, as in the case of the decoloration of 2,4-dinitroanisole[4].

$$k_d=\frac{1}{-0.4343(t-t_{0d})}\log\frac{d}{d_{0d}} \quad (2)$$

Here d_{0d} is the value of d after t_{0d}. By taking $t_{0C}=2$ and $t_{0d}=12$ in Eqs. 1 and 2, the values of k_C and k_d at 25°C are calculated respectively, as indicated in Table I.

TABLE I

t(min.)	k_C(mol^{-1}·sec^{-1})	t(min.)	k_d(sec^{-1})$\times10^3$
3	101	25	3.35
4	109	30	3.71
5	99.8	35	3.61
6	104	40	3.37
7	99.7	45	3.47
8	103	55	3.26
	mean 103	65	3.54
t	$k_d\times10^3$	t	$k_d\times10^3$
75	3.64	155	3.64
88	3.71	165	3.68
95	3.64	180	3.64
105	3.68	195	3.64
115	3.64	205	3.61
125	3.61	225	3.57
136	3.64	240	3.54
145	3.75		mean 3.57

The means of k_C and k_d are 103 mol^{-1}·sec^{-1} and 3.57×10^{-3} sec^{-1}, respectively. In the decoloration reaction sodium hydroxide may probably interact with the colored species, because the higher the concentration of alkalies contained, the faster disappear the colors of the complexes of polynitrobenzenes with alkalies[4,6].

It is in progress to investigate the effect of the concentration of sodium hydroxide of the rate of the decoloration reaction, and to obtain energies of activation for the coloration and docoloration.

The author is particularly indebted to Professor Y. Nomura for his suggestion and helpful discussions.

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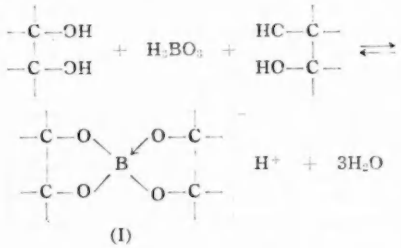
Organic Spot Tests. II. Detection of 1,2-Dihydroxy Compounds (Differentiation of Polyhydroxy Compounds)

By Yujiro NOMURA

(Received July 7, 1959)

The micro detection of acid substances by the color reaction with the mixed solution of sodium sulfanilate, sodium nitrite and α-naphthylamine in aqueous alcohol or dioxan[1] has been developed to a new method of detection of 1,2-dihydroxy compounds.

Boric acid is so weak that the orange to orange red color begins to appear only in 10~15 min. after adding it to the reagent. It has long been known that addition of polyhydroxy compounds, e.g., glycerol, sorbitol and mannitol, to boric acid raises the acidity[2] and thus this weak acid can be titrimetrically determined[3]. This is due to the co-ordinate complex ester (I)[4] of boric acid with 1,2-dihydroxy compounds as follows:



(I)

It has been found that boric acid behaves as a strong acid in the presence of a 1,2-dihydroxy compound also in the above-mentioned reaction to give immediately an intense coloration and that boric acid reciprocally makes it possible to detect 1,2-dihydroxy compounds by the same color reaction. Thus, ethylene glycol, propylene glycol, glycerol and other various polyhydroxy compounds with adjacent hydroxyl groups gave positive reactions with the reagent in the presence of boric acid but trimethylene glycol was indifferent. Catechol also gave a positive reaction, while resorcinol and hydroquinone gave no reaction.

peri-Dihydroxy derivatives of naphthalene behave similarly in this new color reaction. Namely, disodium chromotropate (1,8-dihydroxynaphthalene-3,6-disulfonate) gave the same coloration when the above method was applied.

In the case of a polyhydroxybenzoic acid, its small quantity is evaporated to dryness with one drop of ammonia water in a microcrucible on a water bath and then it may be tested. In this way, 2,3-dihydroxybenzoic acid and gallic acid gave an intense red color, but 2,4-, 2,6- and 3,5-dihydroxybenzoic acids did not.

Accordingly the reaction described above gives a new method of detecting the presence of two hydroxyl groups in 1,2-positions.

General Procedure of the Test.—Several drops of the reagent solution are placed in a depression of a spot plate. A small amount of boric acid is added to it and stirred with a glass rod. One drop of the test solution or a pinch of the solid sample is added to it. An immediate orange red color indicates the presence of a compound with two or more adjacent hydroxyl groups. A blank test without addition of the sample, is recommended if only a small amount of a 1,2-dihydroxy compound is suspected. An acid substance which gives a positive reaction with the reagent solution alone (without the addition of boric acid) must be treated with ammonia water as in the case of the polyhydroxybenzoic acids before the present method is applied.

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1) Y. Nomura, This Bulletin, **32**, 536 (1959).
2) L. Vignon, *Compt. rend.*, **78**, 148 (1874); G. Bouchardat, ibid., **80**, 120 (1875); D. Klein, ibid., **86**, 526 (1878); **99**, 144 (1884).
3) W. Horsch, *Anal. Abstr.*, 2531 (1957).
4) Cf. J. Böeseken, "Advances in Carbohydrate Chemistry", Vol. 4, Academic Press, Inc., New York (1949), p. 193–210.

Measurement of Infrared Dichroism for the Crystal of Lauric Acid in the CsBr Region

By Takehiko Shimanouchi and Michio Kawano

(Received July 9, 1959)

For the measurement of infrared dichroism the silver chloride transmission polarizer is ordinarily used. However, in the region below 20 μ its performance is not satisfactory owing to its poor transmittance. For the purpose of measuring dichroism for saturated long chain monocarboxylic acids in the range from 600 to 350 cm^{-1} we tested a transmitting polarizer in which six polyethylene films are used instead of silver chloride plates.

The result is very satisfactory and the spectra for lauric acid are shown in Fig. 1. This polarizer is also used in the NaCl region except those about the 2900, 1475, 1375 and 720 cm^{-1} absorptions of polyethylene. In Fig. 2 the dichroism for the oriented crystals of lauric acid in the region from 1300 to 900 cm^{-1} measured by the polyethylene polarizer is given. For the purpose of comparison the same dichroism measured by a Perkin-Elmer AgCl polarizer is shown in Fig. 3. The result indicates that the performance of the present polarizer is as satisfactory as that of the AgCl polarizer.

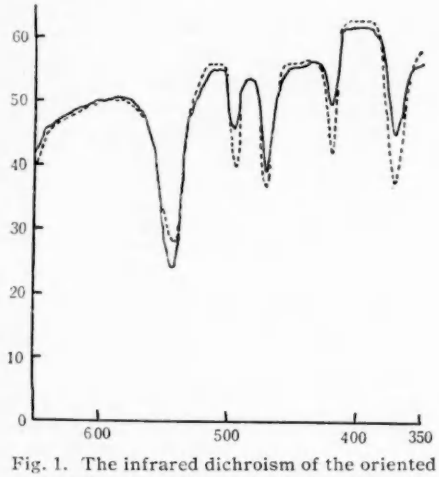

Fig. 1. The infrared dichroism of the oriented crystals of lauric acid (C form) in the CsBr region measured by a polyethylene polarizer.

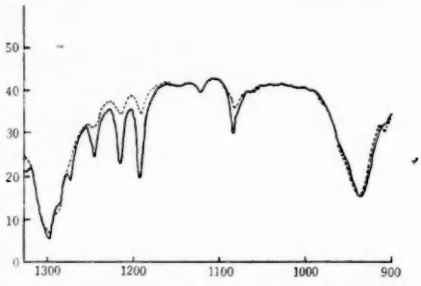

Fig. 2. The infrared dichroism of the oriented crystals of lauric acid (C form) in the NaCl region measured by a polyethylene polarizer.

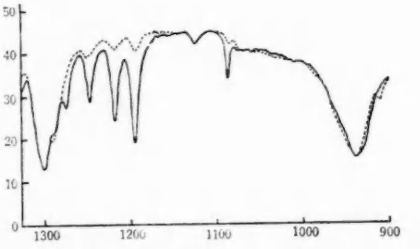

Fig. 3. The infrared dichroism of the oriented crystals of lauric acid (C form) in the NaCl region measured by an AgCl polarizer.

The thickness of the polyethylene film used was 0.02 mm. and an incline of approximately 60 degrees of the films gave the best perfomance. The measurement was made by a Perkin-Elmer Model 21 spectrometer equipped with NaCl or CsBr prism.

In Figs. 1, 2 and 3 the dotted and the full lines give the spectra for the incident light polarized along the *a*- and *b*-axes of the crystal, respectively. It is interesting to note that the four lines in the range from 350 to 500 cm^{-1} given in Fig. 1 have the opposite dichroism to that of the equally spaced progression of bands found in the region from 1180 to 1350 cm^{-1}. The interpretation of the result will be reported afterwards.

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Added in Proof:
Recently H. Yoshinaga, S. Fujita, Y. Yamada and A. Mitsuishi have made a polyethylene film polarizer and used this for the region measured by the far-infrared grating spectrometer (Symposium on Molecular Structure and Spectroscopy at Columbus, June, 1959).

Paramagnetic Resonance Absorption in Solutions of the Sodium Adducts of Isoprene

By Keiji Kuwata, Kazuo Morigaki and Kozo Hirota

(Received July 9, 1959)

It has been found already by Weissman[1a] and others[2] that paramagnetic resonance absorption spectra are observed in the solutions of the sodium adducts of polynuclear aromatic hydrocarbons, e.g., naphthalene, phenanthrene, naphthacene, etc., and also of benzene derivatives[1b]. Recently, the list of such substances has been enlarged to another kinds of adducts by the present authors, i.e., the adducts of polymerizable vinyl monomers, such as styrene[3], α-methylstyrene[4], 1, 4-diphenylbutadiene[5].

However, since all the above hydrocarbons have one benzene ring at least, it will be interesting to investigate if the adducts of polymerizable vinyl monomers without aromatic rings have the same character. Using the method of preparation as described elsewhere[3], Na-adduct of isoprene was obtained as the solution of tetrahydrofuran. The sample colored brownish yellow, maximum absorption being near 375 mμ. Detailed discussion on the structure of the adduct will be published in a separate paper[6].

Measurement of paramagnetic resonance absorption on the sample gave an affirmative result for the object of the present research. A spectrum of the adduct of isoprene is shown in Fig. 1. Hyperfine structure of the spectra can be explained if a radical anion is assumed to exist, but detailed discussions will appear in future.

The writers express sincere thanks to Professor Junkichi Itoh of Osaka University who gave them much suggestion and convenience in the present research. A part of the expense for the research has been defrayed from a grant given by the Ministry of Education, to which the authors' thanks are due.

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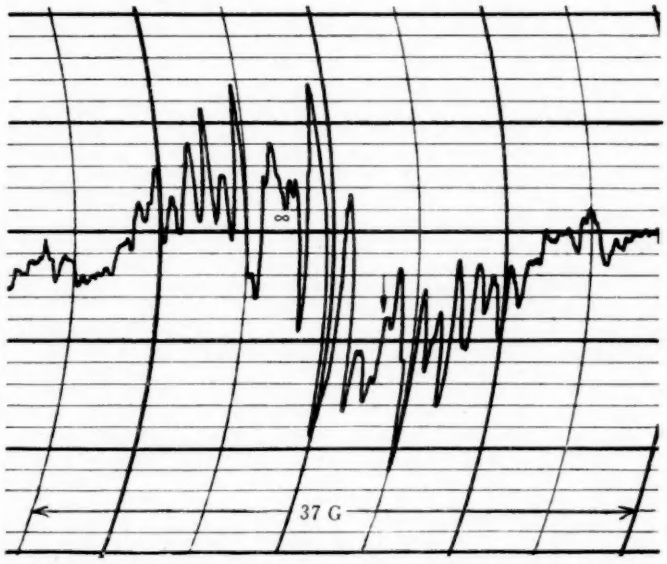

Fig. 1. Derivative of paramagnetic resonance absorption of Na-adduct of isoprene. (g=2.0026)

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2) A. Carrington, F. Dravnieks and M. C. R. Symons, *J. Chem. Soc.*, **1959**, 947.
3) K. Hirota, K. Kuwata and K. Morigaki, This Bulletin, **31**, 538 (1958); **32**, 90 (1959).
4) K. Morigaki, J. Itoh, K. Kuwata and K. Hirota, "*Sen-i-Kagaku Kenkyusho Hokoku*" (Osaka Univ.), **12**, in press (1959).
5) Unpublished results.
6) K. Kuwata, to be published in This Bulletin.

The Synthesis of dl-4(-3-Furyl)-1-methyl Quinolizidine; Demethyl Analogue of Deoxynupharidine

By Munio KOTAKE, Ichiro KAWASAKI, Tadashi OKAMOTO, Shiro KUSUMOTO and Takeo KANEKO

(Received June 30, 1959)

In 1956, structure (I) was assigned by Kotake, Kusumoto and Ohara[1] to deoxynupharidine; an alkaloid isolated from the roots of *Nuphar japonica* DC. A synthesis of *dl*-4(-2-furyl)-1-methyl quinolizidine is now reported which establishes the synthetic routes to the *dl*-deoxynupharidine*. The stages involved in the synthesis are as follows:

Compound II[2], b. p. 133°C/10^{-2} mmHg; III, (62%) b. p. 130°C/10^{-2} mmHg, I. R. bands at 1645 (amide), 1735 cm^{-1} (ester). *Anal.* Found: C, 64.78; H, 8.89; N, 5.80. Calcd. for $C_{13}H_{21}O_3N$: C, 65.24; H, 8.85; N, 5.85%; IV, (95%) m. p. 102~106°C. *Anal.* Found: C, 53.69; H, 9.13; N, 6.20. Calcd. for $C_{10}H_{19}O_2N$-HCl: C, 54.17; H, 9.09; N, 6.33%; V, (48%) b.p. 154°C/10^{-3} mmHg, I.R. bands at 875, 1505, 3110 (furan), 1573 (conjugated furan), 1625 (amide), 1735 cm^{-1} (ester). *Anal.* Found: C, 65.94; H, 8.24; N, 4.51. Calcd. for $C_{17}H_{25}O_4N$: C, 66.42; H, 8.20; N, 4.56%; VI[3], (56%) b. p. 81~84°C/10^{-3} mmHg, I. R. bands at 875, 1505, 3110 (furan), 1588 (conjugated furan), 1640 cm^{-1} (double bond); VII, (50%) b. p. 87~89°C/10^{-2} mmHg. Perchlorate, m. p. 193~194°C. *Anal.* Found: C, 52.56; H, 6.82; N, 4.34. Calcd. for $C_{14}H_{21}ON \cdot HClO_4$: C, 52.57; H, 6.93; N, 4.38%. Picrate, m. p. 172~174°C. *Anal.* Found: C, 53.30; H, 5.40; N, 12.79. Calcd. for $C_{20}H_{24}O_8N_4$: C, 53.57; H, 5.39; N, 12.50%.

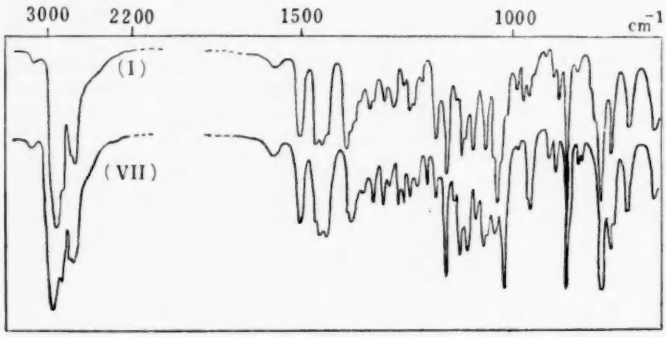

Fig. 1.

The I. R. spectra of compound VII are similar to that of the deoxynupharidine as indicated in Fig. 1.

The authors wish to express their thanks to Professor Takeo Sakan, Professor Takashi Kubota and Professor Yasuhide Yukawa for their encouragement throughout this work.

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* The synthesis of *dl*-deoxynupharidine was reported elsewhere.

1) M. Kotake, S. Kusumoto and T. Ohara, *Ann.*, **606**, 148 (1957); This Bulletin, **29**, 157 (1957); *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **77**, 1302 (1956); **78**, 488 (1957).

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